DOCTOR OF PHILOSOPHY

Rapid assessment of the potential chloride resistance of structural concrete

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RAPID ASSESSMENT OF THE POTENTIAL CHLORIDE RESISTANCE OF STRUCTURAL CONCRETE

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A Thesis Presented in Application for the Degree of Doctor of Philosophy

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DECLARATION

I hereby declare that I am the author of this Thesis, that the work of which it is a record, has been carried out by me, all references cited have been duly consulted and it has not been previously presented for a higher degree.

Zahiruddin Fitri Abu Hassan

CERTIFICATE

This is to certify that **Zahiruddin Fitri Abu Hassan** has completed this research under our supervision, and that he has fulfilled the conditions of Ordinance 14 of the University of Dundee, so that he is qualified to submit this Thesis in application for the Degree of Doctor of Philosophy.

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PUBLICATIONS

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ABSTRACT

This present study benchmarked the chloride resistance of concretes mixes at the limit state of BS 8500-1:2006 using the newly published CEN TS12390-11. Of the three allowed methodologies, the immersion test was carried out. At least two water-cement ratios were produced for each mix design to enable normalisation of the results. The performance of concrete was compared on the basis of equal compressive strength, i.e. 40 and 50 N/mm^2 and an equal water-cement ratio of 0.45. In addition to the CEN TS 12390-11:2010, rapid test methods NT Build 492 and a steady-state migration test UNE 83987:2009 were also conducted. Selected concretes were also tested for cyclic wetting in artificial sea water and evolution of chloride diffusion over the test period. The ageing factor of concrete mixes, which describes the development of diffusion coefficient (D) from the unsteady to steady-state determined from this research was compared with those reported in The Concrete Society Technical Report 61. Test specimens for highway exposure were also produced for future research work.

CEN has just agreed and published (at the time of the writing of this thesis) a test methodology for chloride resistance as a technical standard (CEN, 2010). The test method underpins the equivalent durability performance approach. Therefore, the use of this test was investigated in terms of evolution of the chloride diffusion, and effect of cyclic wetting and drying in artificial seawater exposure. As the test method is slow, (3 months to complete), other rapid test methods were also studied on the same specimens. The results from these tests were compared to look for the possibility of having a faster test methodology for chloride durability.

Overall, the results showed that concrete mixes at the limiting value of BS 8500-1:2006 have a wide range of performance between 0.3×10^{-12} m^2/s and 20×10^{-12} m^2/s regardless of the test methods. Ranking of concrete according to performance shows that this changes with age. This is the same for all test methods although the rate of change is different between different test methods. However, the ranking of concrete at equal compressive strength and equal water-cement ratio follows the general order of (from best to worst) ggbs> fly ash> silica fume> limestone> CEM I. It was also postulated that there is a limit to the benefit of reducing water-cement ratio to improve durability. This is because of at very low water-cement ratio, concrete may develop autogenous cracking that is detrimental to the porosity.

Using the CEN TS 12390-11:2010 it was found that CEM I, fly ash and silica fume mixes follows the same ageing factor proposed by Concrete Society Technical Report 61 although ggbs shows a different ageing factor. The improvement of ggbs quality was attributed to this change. It was also found that 90 days test duration was optimum as a shorter period risks giving a non stable diffusion rate whilst longer than 90 days shows insignificant change in D_{nss} values. Exposure of selected concrete specimens to cyclic wetting and drying in artificial seawater elevated to 1 M NaCl equivalent shows reduced chloride diffusion. However, the mechanism controlling this is not clear.

The thesis showed that some of the limiting value requirement for BS 8500-1:2006 does not meet the durability requirements for chloride resistance. There are some concrete mixes recommended that performs poorly in testing. The research reported also provides further understanding of the new CEN TS 12390-11:2010 in terms comparative ranking of cements up to the point of comparative performance between other tests methods. Validation of the ageing factor for chloride durability is also provided as well as the need for updates in the age factor values due to changes in the nature of cements.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

GLOSSARY, ABBREVIATIONS AND NOMENCLATURE

BCA — British Cement Association

Benchmark — Comparison of a concrete based on a reference mix

BS 8500 — Concrete - Complementary British standard to BS EN 206-1. Part 1 covers the method for specification and guidance for the specifiers whilst Part 2 covers specification for the constituent materials and concrete.

BS EN 206-1 — Concrete - Part 1: Specification, performance, production and conformity is the main standard for concrete production for European member states.

BSI — British Standards Institution

CEN — European Committee for Standardization (Comité Européen de Normalisation)

CEN/TC104 — Construction product directive under CEN for concrete and related products

CEN/TC51(CEN/TC104)/JWG12/TG5

Task Group 5 is a technical body within the Joint Working Group 12 (JWG12) tasked with the evaluation of performance related test methods to assess concrete's resistance to forms of attack associate with corrosion of steel reinforcement.

CEN/TC51 and CEN/TC104 are the construction product directives under CEN for cement and building limes, and concrete and related products respectively.

CH — Calcium hydroxide (cement chemist notation). Chemical formula is $Ca(OH)_2$

C_i — Initial chloride content in a powder sample, percentage by mass of concrete

Cl^- — Chloride ion

Compressive strength

The compressive strength in this thesis refers to compressive strength obtained from 100 mm cube specimens. EN 206-1 and BS 8500-1:2006 lists concrete strength as class (C40/50) where C40 refers to cylinder specimens and 50 refers to cube specimens

C_s — Chloride content in the surface of concrete, in a powder sample, percentage by mass of concrete

CSTR61 — Concrete Society Technical Report 61

D — Diffusion coefficient. The use of this abbreviation depended on the context of what is being referred to. In general when the term D is used, the diffusion coefficient referred to cannot be attributed to a specific diffusion parameter

D_{nss} — Diffusion coefficient measured from non steady-state diffusion test referred to in this thesis as CEN TS 12390-11:2010 unless stated otherwise

D_{nssm} — Diffusion coefficient measured from non steady-state migration test referred to in this thesis as NT Build 492 unless stated otherwise

D_{ssm} — Diffusion coefficient measured from steady-state migration test referred to in this thesis as UNE 83987:2009 unless stated otherwise

FA/fa	Fly ash
GGBS/ggbs	Ground granulated blastfurnace slag
ICRI	International Concrete Repair Institute, Illinois, US
IETcc	Eduardo Torroja Institute for construction Sciencie, Madrid, Spain
l	Litre
LS	Limestone fines
M	Molar
NaCl	Sodium Chloride
OH^-	Hydroxyl ion
PC	Portland cement.
PD	Potential Difference. A test method described by Dhir et al., 1990 to measure diffusion coefficient index of test concrete using the two-cell test principles and uses modified Ficks 1st law equation to arrive at a steady-state chloride diffusion index.
Ranking	Classification of a concrete mix based on a particular order
Reference	Reference concrete in Chapters 4 to 7 refers to CIII/A concrete, 0.5 w/c, 50 N/mm^2 compressive strength at 28 days, designed for 50 mm minimum cover with an intended working life of 50 years. The aggregate used is 20 mm (maximum size) natural gravel. CEM I used is 52.5 R rapid hardening Portland cement. The reference concrete is further described in Section 4.1.2
RILEM	International Union of Laboratories and Experts in Construction Materials, Systems and Structures (Réunion Internationale des Laboratoires et Experts des Matériaux, systèmes de construction et ouvrages)
SF/sf	Silica fume
SRPC	Sulfate resisting Portland cement
w/c	water-cement ratio
wt	weight
XC	Exposure classes for risk of corrosion induced by carbonation defined in BS EN 206-1
XD	Exposure classes for risk of corrosion induced by chlorides other than from sea water defined in BS EN 206-1
XS	Exposure classes for risk of corrosion induced by chlorides from sea water defined in BS EN 206-1

CHAPTER 1. INTRODUCTION

1.1 BACKGROUND

There have been attempts by the standardisation bodies to move the concrete industry from a prescriptive-based approach for concrete durability currently practised to a performance-based approach. In order to achieve this, performance measurement tests that underpin durability have been developed by several researchers and bodies. Understanding the fundamental nature of these tests is important and it has been debated in the European Committee for Standardisation (CEN) over many years.

Similarly, because there are many test methods that give different results, it is important to identify which test or tests are to be adopted as standards and how useful the results are. What has to be established is whether these tests give absolute durability values for concrete thus allowing them to be used in service life modelling or whether they can be used only within a comparative performance index framework. These issues have kept the pace of standardisation of test methods slow amid pressures for a European standard test with regard to chloride resistance (Andrade et al., 2002, Gulikers, 2012).

One of the major durability concerns is reinforcement corrosion due to the diffusion of chloride ion through the concrete causing the breakdown of the passive protective layer. This leads to localised corrosion pitting and acts as an active feed to other corrosion sites (Bertolini et al., 2006). Although this problem is limited to structures near marine environment and de-icing salt situations, the financial cost is high given that these structures are usually associated with the infrastructure. These structures include bridges and crossings that are expensive to build and maintain.

A report by the British Cement Association (BCA) had attributed more than 60% of bridge deterioration mechanism to corrosion of reinforcement due to chlorides (both internal and external) (Jones and BCA, 1997). The size of the concrete repair industry is large (~$10 billion a year - 2004 figure- in the US for chloride and carbonation induced corrosion or ~50% of total repair budget (ICRI, 2004)), and frequently working on structures that have failed to achieve their intended working life.

Research to minimise the impact of chloride-induced corrosion has been going on for decades. The spectrum of research is vast, spanning from material chemistry, structural design and mix combination from the pre-construction side up to protection systems and rehabilitation on the far end of the scale. The direction of research is also heavily influenced by the impact of climate

change and sustainability since one of the biggest producers of CO_2 for the construction sector is Portland cement manufacture.

The general perception has been that durable concrete, in terms of having good chloride resistance properties, comes from high strength and low water-cement ratio concrete. It also comes from utilising more supplementary binder materials, for example fly ash and ground granulated blast furnace slag.

Diffusion of chlorides in concrete varies over time and the rate of diffusion is not constant. This has meant that comparing two concretes for chloride resistance measurement at an early age may not reflect their potential durability performance at a later advanced age. Cementing materials may exhibit different ageing effects due to their differences in chemistry and reaction to exposure conditions.

In order to produce more durable concrete design, a new approach away from the prescriptive methodology as prescribed by BS 8500-1:2006 standards may be proposed to the industry (BSI, 2006a). At the moment, BS 8500-1:2006 specifies concrete based on the environment in which the concrete is going to be exposed. This is known in BS 8500-1:2006 as exposure classes related to environmental conditions. The traditional concept of high strength and low w/c and thus costly concrete design may not be appropriate in responding to the sustainability pressures.

There are several approaches that a designer may pursue in order to achieve the aim of moving away from prescriptive standards methodology. The first is to develop and apply a mathematical service-life-model for structures that are exposed to chloride environments. The modelling route is desirable and pragmatic as the intended working life of concrete structures is often beyond experimental science. However, some quarters of the research community are sceptical to the data used to support the modelling approach.

The equivalent durability approach for concrete specification is also proposed as one way forward for the construction industry in order to achieve sustainability and to break away from the cost of over-design and the environmental impact of over-safe concrete (Harrison, 2008). The equivalent durability concept was proposed by CEN to be introduced in the normalised European Standards EN 206-1 Concrete – Part 1: Specification, performance, production and conformity (BS EN 206-1) for its revision in 2010. It is based on the premise that, if a new concrete has a relatively similar durability to a known reference concrete which has a historically good durability performance, it should equally perform well in a similar environment.

Currently, the equivalent durability approach is entered as an annex in BS EN 206-1:2000 allowing countries with confidence in locally approved test method/s to specify concrete based on performance (BSI, 2000b). The equivalent durability approach will apply to exposure classes codes defined in BS EN 206-1:2000 and, for the time being operate in parallel with the conventional compositional approach. As concrete is a widely used material, a modest improvement in design for sustainability is likely to be significant to the industry as a whole.

BS EN 206-1:2000 specifies two sets of exposure conditions for concrete subjected to chloride action, coded XD1 to XD3 for risk of corrosion by chloride attack by sources other than sea water and XS1 to XS3 for risk of corrosion by chloride attack due to the exposure to sea water. The assessment of durability for chloride is proposed to be based on a natural diffusion test or a rapid migration test to be agreed by the CEN member countries.

1.2 AIM AND OBJECTIVES

The overall aim of this project is to establish the difference between concretes on the basis of chloride diffusion. At a given equal strength and water-cement ratio, there are differences between two concretes. In order to establish this difference, the concrete specimens will be subjected to diffusion tests over time. The main test method selected is the CEN candidate chloride diffusion test, a draft of which is being considered by the CEN committee at the time of this thesis. This test has now been published as CEN TS 12390-11:2010 (CEN, 2010).

Additionally, two other nationally standardised test methods are also tested to compare the performance given by them against the reference test. These are electro-migration tests NT Build 492 (Nordtest, 1995), which is a non steady-state test method in the Nordic countries and the steady-state version of the Spanish UNE 83987 (UNE, 2009).

The specific objectives of this study are to:

i. Comprehensively review the literature of ageing effects.
   The factors that influences ageing and their effect to the resistance of concrete to chloride ingress will be examined, focussing on the current understanding since 2002. Among others, factors such as cement types, water-cement ratio and cement content will be considered.

ii. Undertake a comprehensive laboratory study on ageing effects for exposure classes XD3 and XS3 using the CEN candidate chloride diffusion test.

The experimental work spans 18 months. Within this period, the concrete specimens will be periodically tested to obtain an ageing plot. The robustness of the test method is also tested by extending the exposure period. Additionally, specimens will be tested with NT Build 492, UNE 83987:2009 and with artificial seawater exposure.

iii. Benchmark the chloride diffusion of UK concretes at the limiting values of BS 8500-1:2006 recommended for an intended working life of 100 years.

Mixes will be normalised to a specific equal compressive strength and water-cement ratio. This is to ensure comparison is made on a equal basis. Diffusion coefficient values measured from the test will be overlaid against the age factor proposed in The Concrete Society Technical Report 61 (Bamforth, 2004).

iv. Compare the performance of concrete subjected to the CEN TS 12390-11:2010 with NT Build 492 and UNE 83987:2009.

The performance of all three test methods are to be compared to identify whether the diffusion coefficient and the rank order between test methods are comparable.

1.3 SCOPE OF STUDIES

The study tests concretes recommended in BS 8500-1:2006 for designed concrete at the limiting values of composition in XD3 and XS3 environment for an intended working life of 100 years. These are regarded as the most severe environment for concrete in terms of durability against chloride ingress. Concretes are designed for the nominal cover of 60mm with 20mm maximum aggregate sizes. Table 1.1 and Table 1.2 show the limiting values of the durability recommendation in BS 8500-1:2006 for XD3 and XS3 exposure classes respectively.

Establishing comparative performance is key to the equivalent durability approach. With that in mind, a suitable test method with sound scientific fundamentals is needed to underpin this approach. Establishing this framework is the task taken by CEN TC51(CEN/TC104)/JWG12/TG5 to agree to a standard test method acceptable to the EU countries.

The present study focuses on the then final draft of CEN TS 12390-11:2010, Testing hardened concrete - Determination of the chloride resistance of concrete, unidirectional diffusion. Investigation involves the performance of concrete with respect to their chloride resistance as well as other factors that may influence the outcome of this test. This technical specification has been

published and the method is now undergoing a round-robin test to determine reproducibility and repeatability of which the University of Dundee is taking part.

However, it is felt that the candidate CEN test method is still too slow and not suitable as a practical solution to the needs of practising engineers tackling design requirement in new infrastructure projects. The rapid test methods based on electro-migration are not being addressed as member countries could not agree on the fundamental physics of the process in relation to concrete properties.

The test programme is then designed to compare the candidate test method against two popular test methods that have been standardised in Spain and the Nordic countries respectively. The comparison is made against the ranking of the different concrete mixes to see whether the ranking based on the CEN TS 12390-11:2010 test can be replicated in a more rapid test.

Another important facet of the problem of chloride resistance is the aspect of reinforcement corrosion. However, reinforcement corrosion, although an integral part of the deterioration process, will not be emphasised in this thesis. This is because it is the view that once chloride ion concentration has passed a threshold at the reinforcement, the propagation and time to failure is relatively quick. The best chance to get to the intended working life is at getting the bulk concrete resistant enough thus delaying the ingress of chloride to the reinforcement steel.

Studying the concrete at the limiting values gives an indication of the basic durability coefficient as a benchmark of what producers are aiming for based on BS 8500-1:2006. By applying the durability coefficient based on CEN TS12390-11 to the ageing factor model from the Concrete Society Technical Report 61 (CSTR61) written by Phil Bamforth (2004), may serve as an indicator of whether the durability coefficient equivalent of the current standard of limiting value specification may be regarded as being enough to cater for the intended 100 year working life.

The contribution of this thesis is to present an empirical analysis of the current limit value requirements of concrete recommended by the current BS 8500-1:2006 standard for its chloride diffusion coefficient as it stands today. It will also try to show that with respect to sustainability, prescriptive standards methodology needs to be abandoned in favour of performance-based approach.

Table 1.1 XD3 exposure class mix design for 60 mm nominal cover (BSI, 2006a)

Cement/combination	Strength class	Max w/c	Min cement, kg/m^3
CEM I, CIIA, CIIB-S	C40/50	0.40	380
CIIB-V, CIIIA	C28/35	0.50	340
CIIIB, CIVB-V	C25/30	0.55	320

Note: C indicates that a cement combined at the mixer

Table 1.2 XS3 exposure class mix design for 60 mm nominal cover (BSI, 2006a)

Cement/combination	Strength class	Max w/c	Min cement, kg/m^3
CEM I, CIIA, CIIB-S	C45/55	0.35	380
CIIB-V, CIIIA	C28/35	0.50	340
CIIIB, CIVB-V	C25/30	0.50	340

Note: C indicates that a cement combined at the mixer

1.4 THESIS OUTLINE

The thesis is organised as follows. After this introductory chapter, a critical review of the literature is carried out in Chapter 2. The review dwells on the latest understanding of chloride transport properties and the important phenomenon of chloride binding that contributed to the ageing factor. It will also touch on the other factors that influence resistance of concrete to chloride ingress. Current durability standards and guidance documents are also reviewed before finally commenting on the available chloride tests and the development of the test method used in the current study.

Chapter 3 details the experimental work undertaken for this study and covers all the concreting materials and their properties, mix proportions, procedures and description of the test methods.

Chapters 4 to 8 are the tabulation of the test results, important findings and comments.

Discussion and conclusions on the findings are discussed in Chapters 9 and 10. These chapters will also list the limitations and implication of this research and recommendations for future works.

CHAPTER 2. LITERATURE REVIEW

2.1 DURABILITY IN CHLORIDE ENVIRONMENT

Although chloride ingress itself is not harmful to concrete, it can attack the steel reinforcement causing pitting corrosion as a result of the reaction between chloride ions and the steel. Chloride-induced corrosion is the most common defect in structures that come in contact with chloride ions either by de-icing salt exposure or sea water (Jones, 1997, Baroghel-Bouny et al., 2007a).

This study concerns the assessment of the European test methods used to measure chloride ingress resistance in these two environments. It is therefore imperative that the established body of knowledge on chloride ingress into concrete is first revisited and summarised before focussing on the standard European test methods for which the framework is being established. Finally the direction of European standards with regards to chloride resistance that influences the Equivalent Durability Performance principle is discussed.

Due to the vast volume of publications in the field of study, this review focussed especially on the literature published after the Third international RILEM workshop on testing and modelling chloride ingress into concrete, held in Madrid, 2002. Publications by key European research workers are given emphasis to further scale-down the literature. In addition, highly cited literature from key workers from other regions are also covered.

2.1.1 Kinetics of chloride ingress

Chloride ingress into concrete results from multiple fluid transport mechanism affecting concrete in its hardened state. Although the main sources of chloride are either seawater or de-icing salt, up until the 1970's calcium chloride ($CaCl_2$) was regularly added to concrete to accelerate the setting time. The physical actions of ingress are identified as diffusion due to the difference in concentration gradient and sorption due to capillary action (Neville, 1995). Other physical actions were also attributed such as convection (Andrade, 1993, Wong et al., 2001), permeation (Stanish et al., 2000) and condensation (Nagataki et al., 1993).

Within the surface zone in a marine or de-icing salt environment, chloride ingress is a mixture of several transport mechanisms, be it sorption and permeation of water containing chloride or diffusion of the chloride ions itself. The surface zone is very much influenced by the external environment and this in turn influences the rate of fluid transport. In a non-saturated state of

alternating wetting and drying cycles coupled with wind blowing in the marine atmosphere, concurrent actions may exacerbate ingress (Climent et al., 2002).

Permeation of chloride induced by pressure gradient may be significant in structures in saline water, for example experienced by submerged tunnels (Koenders et al., 2009).

There are two dominant processes that lead to the penetration of chloride into concrete and they are described below.

2.1.1.1 Diffusion of chloride ion

As bulk concrete is rarely dry, chloride ions from external sources can move inwards from the surface of concrete through diffusion in the pore water. The term ionic diffusion is used in this instant as chloride ions are moving in a saturated or partially saturated pores of the hardened cement paste (Neville, 1995).

The rate of diffusion is controlled by water-cement ratio, concrete strength, aggregate types (Dhir et al., 2004, Dhir et al., 2006), binding capacity/cement type, temperature (Bertolini et al., 2006) and degree of pore saturation (Neville, 1995). In addition, diffusion coefficient changes with age because of the change in pore system with time due to hydration (Neville, 1995).

At depths greater than the paste rich outer zone of approximately 0.5 times the size of the coarse aggregates (Poulsen and Mejlbro, 2006), ingress of chloride is dominated by diffusion as beyond this depth the concrete pore system is rarely dry (Stanish et al., 2000).

2.1.1.2 Absorption of water containing chloride

Penetration of water containing chloride into concrete element as a result of capillary action is often confused with permeability. The term concrete permeability actually means movement of water through saturated concrete under a pressure differential (McCarter et al., 1992). Absorption is dominant in the surface zone where concrete is unsaturated. Absorption properties of a concrete are affected by the way it is being tested and cannot be used to measure concrete quality. However, most good quality concrete has an absorption value of less than 10% by mass (Neville, 1995). The ISAT (Initial Surface Absorption Test) is a practical test to measure the absorption characteristics of the surface zone of concrete (BSI, 1996). The ISAT test is limited due to specific specimen drying preconditioning that can influence the measured values although it is useful to compare the effectiveness of curing on the surface zone (Neville, 1995).

2.1.2 Exposure environments and chloride ingress

The kinetics of chloride ingress varies between different exposure zones. Especially in marine environment, several exposure zones have been identified. As a result, EN 206 and BS 8500-1:2006 classified these zones separately. Table 2.1 shows the separated exposure zone according to EN 206 and further detailed in BS 8500-1:2006.

Figure 2.1 shows the range of different exposure condition that can be encountered by a single concrete member in a marine environment. Within a single member, but at different locations the severity of exposure is different. Submerged zone which is constantly under water may survive with a higher chloride concentration without significant corrosion because of the lack of oxygen to drive the corrosion process (Bertolini et al., 2006).

On the other hand, the inter tidal zones and the splash zone along the height of a structure are more prone to deterioration due to the aggressive chloride ingress (Buenfeld and Newman, 1984, Mehta, 1991). The alternating wetting and drying cycles in the tidal zone allows ingress of seawater followed by evaporation of pure water leaving the salt behind (Neville, 1995). It has been established that the dynamic nature of the splash zone where cyclic wetting and drying coupled with evaporation and exposure to wind causes chloride to travel further inwards due to the multiple transport process.

It is stipulated from the limiting values requirement laid out in BS 8500-1:2006 that XS3 environment (Tidal, splash and spray zones) is regarded as the most severe. Minimum cover depth for CEM I, CII/A, CII/B-S and SRPC starts at 60 mm with minimum 380kg/m^3 cement, 0.35 maximum water-cement ratio and 55 N/mm^2 compressive strength (BSI, 2006a).

2.1.3 Chloride induced corrosion

The principal problem with chloride ingress into reinforced concrete is the breakdown of the passive protective film in the form of gamma ferric oxide (γ-Fe_2O_3) that adheres to the steel by the diffusing chloride ion. In the presence of moisture and oxygen, corrosion occurs.

The pitting corrosion reaction due to chloride ingress is aggressive as areas where the passive film is broken down, act as anodes and when connected to surrounding cathodic regions by the pore water (the electrolyte) an electrochemical cell is formed. Positively charged ferrous ions flow to the cathodic region increasing the chloride content of the pit as the negatively charged chloride ions migrate to the anodic region. The hydrolysis of ferrous ions forming ferric hydroxide increases the acidity within the pitting zone and is consequently converted to rust. The autocatalytic cycle

accelerates corrosion as more chloride ions are concentrated at the pit (see Figure 2.2) (Mehta, 1991, Neville, 1995, Hobbs, 1998, Bertolini et al., 2006).

BS EN 206-1 placed a limit of 0.4% maximum chloride content by mass of cement where steel reinforcements are used, modern day concrete are designed to generally have negligible chloride content as a result of better understanding of its detrimental effect to steel reinforcement. However, chloride can still be present in marine dredged aggregates.

Table 2.1 Table describing exposure classes related to chloride environment in EN 206:1 (BSI, 2000b)

Class designation	Description of the environment	Informative examples where exposure classes may occur
3. Corrosion induced by chloride other than from sea water		
Where concrete containing reinforcement or other embedded metal is subject to contact with water containing chlorides, including de-icing salts, from sources other than from sea water, the exposure shall be classified as follows: NOTE Concerning moisture conditions, see also section 2 of this table.		
XD1	Moderate humidity	Concrete surfaces exposed to airborne chlorides
XD2	Wet, rarely dry	Swimming pools. Concrete exposed to industrial waters containing chlorides
XD3	Cyclic wet and dry	Parts of bridges exposed to spray containing chlorides. Pavements. Car park slabs.
4. Corrosion induced by chlorides from sea water		
Where concrete containing reinforcement or other embedded metal is subject to contact with chlorides from sea water or air carrying salt originating from sea water, the exposure shall be classified as follows:		
XS1	Exposed to airborne salt but not in direct contact with sea water	Structures near to or on the coast
XS2	Permanently submerged	Parts of marine structures
XS3	Tidal, splash and spray zones	Parts of marine structures

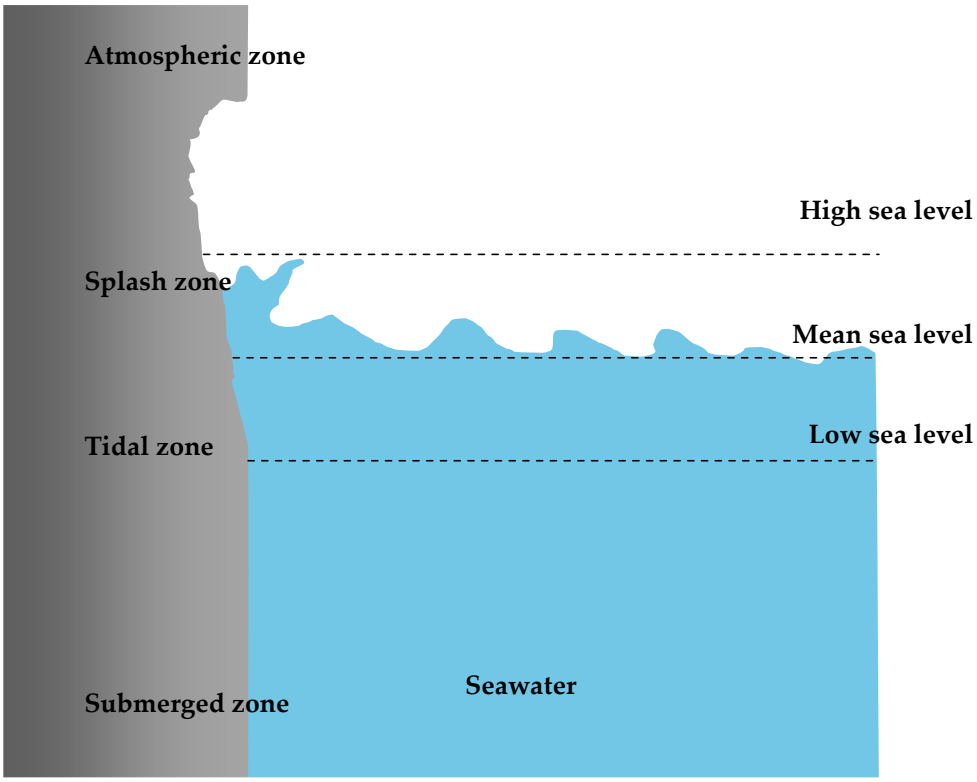


Figure 2.1 Exposure zones for XS3 environment (Bertolini et al., 2006)

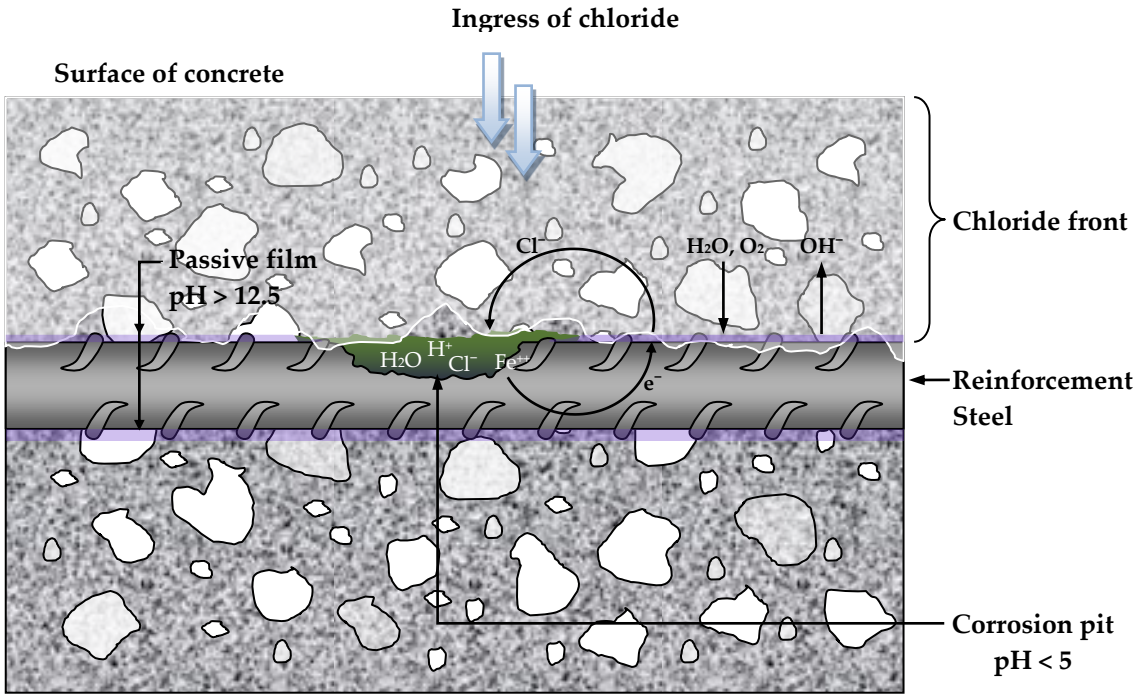


Figure 2.2 Schematic representation of pitting corrosion of steel in concrete

2.1.4 Chloride ingress in carbonated concrete

It is generally acknowledged that only free chloride participates actively in the corrosion process of steel reinforcement (RILEM, 2002, Siegwart et al., 2003) although there are suggestions that bound chloride have a role to play in the dissolution of the passive film that protects reinforcement (Glass and Buenfeld, 2000, Glass et al., 2000). That is why high levels of supplementary cementing materials such as fly ash, ggbs and metakaolin are regularly used where concrete is designed for chloride environment because of their chloride binding capacity. However, the choice of cement materials for the chloride exposure has to be balanced where the exposure environment does include risk from carbonation-induced corrosion (Jones et al., 2003). Carbonation releases bound chloride into the pore system allowing it to participate in the corrosion process.

The optimum humidity range where carbonation occurs is between 60% to 75% (Khanna, 2009). In this range, there is sufficient moisture and relative ease for the passage of CO_2 to react within the pore system to form carbonic acid. The reaction between CO_2 and $Ca(OH)_2$ that maintains the high pH of the pore system destabilises the thin passive oxide film that protects the steel reinforcement from corrosion (Neville, 1995). The reaction that takes place in aqueous solution is written by Bertolini et al., (2006) as:

$$CO_2 + Ca(OH)_2 \xrightarrow{H_2O,\ NaOH} CaCO_3 + H_20 \qquad \textbf{Equation 2.1}$$

The consequence of this reaction is, (1) the steel reinforcement will start to corrode; and (2) as the pH of the pore solution drops to below pH 12.5, bound chloride in the form of Friedel's salt are liberated into the pore solution causing an aggressive attack on the steel via,

$$3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O \rightleftarrows 4Ca^{2+} + 2Al(OH)_4^- + 2Cl^- + 4OH^- + 4H_2O$$

Equation 2.2

It is known that at an equal strength, high replacement levels of fly ash and ggbs give higher carbonation rates compared to CEM I (Bertolini et al., 2006). It has been argued however, that good curing and a dense microstructure are important factor to reduce carbonation by shutting down the pore system and reducing ingress of CO_2.

2.2 UNDERLYING THEORY FOR CHLORIDE DIFFUSION IN CONCRETE

The use of Fick's laws of diffusion to describe the diffusion of chloride in concrete first appeared through the work of Mario Collepardi and his colleagues circa 1970's (Poulsen and Mejlbro, 2006). In a steady state flow, the transport of chloride ions through a sectional unit area of concrete per unit time is proportional to the concentration gradient of the chloride ion. This is Fick's first law of diffusion (Crank, 1956):

$$\boldsymbol{F = -D \cdot \frac{\partial C}{\partial x}} \qquad \textbf{Equation 2.3}$$

Where,

$\frac{\partial C}{\partial x}$ = concentration gradient, kg/m^3 or mol/m^3. C is chloride concentration or flux potential and x is depth of penetration, m

F = mass transport rate of chloride or flux, kg/m^{2}s or mole/m^{2}s.

$-D$ = diffusion coefficient, m^2/s. The negative sign (−) is because chloride diffusion occurs in the opposite direction of the increasing chloride ion concentration and D is constant, i.e. $D = D_0$.

However, chloride ingress into concrete is dependent on time and space. The change of chloride concentration per unit time along the x-axis is equal to the change of flux per unit length (Poulsen and Mejlbro, 2006). Fick's second law of diffusion is used in this instance (Crank, 1956):

$$\boldsymbol{\frac{\partial C}{\partial t} = D_0 \cdot \frac{\partial^2 C}{\partial x^2}} \qquad \textbf{Equation 2.4}$$

Where,

C = chloride concentration, mol/m^3

t = time, seconds

x = depth of penetration, m

D = diffusion coefficient in space and time, m^2/s

This law is derived by applying Fick's first law and the mass balance equation.

In the case of instantaneous planar source in a semi-infinite media, two critical assumptions are made. These are constant surface concentration and no other source of diffusion substance present (Andrade, 2002, Climent et al., 2002). Thus the initial conditions are:

i. Constant amount of diffusing m substance

$$\boldsymbol{m = \int_0^{\infty} cdxt \geq 0} \qquad \textbf{Equation 2.5}$$

ii. There is no diffusing substance far from the surface

$$\boldsymbol{C = 0 \text{ for } x = \infty \text{ and } t \geq 0} \qquad \textbf{Equation 2.6}$$

iii. Initially all the diffusing substance is at the surface

$$\boldsymbol{C = 0 \text{ for } x > 0 \text{ and } t = 0,} \qquad \textbf{Equation 2.7}$$

$$\boldsymbol{C = \infty \text{ for } x = 0 \text{ and } t = 0} \qquad \textbf{Equation 2.8}$$

Bertolini et al., (2006) had commented that the theoretical assumptions that describes the apparent diffusion kinetics are rarely met in real structures. In most instances, only in completely submerged marine structures that the transport of chloride ion is diffusion driven. Even then, there are other diffusing ions in the system. For structures in the splash and tidal zone, chloride ingress varies according to the effect of the environment and there are multiple transport mechanisms in place.

The mathematical solution of Fick's second law of diffusion has been extensively used to develop mathematical model of chloride ingress. Apart from Collepardi et. al., other models that use this approach are Takekawa and Matsumoto, 1988, LIGHTCON (Maage et al., 1994), Mejlbro's φ_ρ-function, 1996, and HETEK (Nilsson et al., 1997). These models have been briefly explained in a report by Frederiksen et al. (2008). Angst et al., (2009) commented that service life modelling requires the critical chloride content parameter and the magnitude of this value is still unresolved .

However, if taken strictly, Fick's laws and their variants are valid for non-ionic diffusants only. For ionic diffusants the effect of the electric field should be taken into account expressed by Nernst-Planck or Nernst-Einstein equations (Černy and Rovnanìkovà, 2002).

The solution of Fick's second law of diffusion is also used to determine the apparent chloride diffusion coefficient of concrete obtained from structures and chloride penetration test method. This will be detailed later in section 2.8, Non Steady-State Diffusion Tests.

Diffusion coefficient D, from Equation 2.4 is considered as a parameter independent of time, i.e. it is constant throughout the diffusion period. However, results from laboratory studies and field exposure show that this is not the case. Concrete resistance actually improves over time as the hydration processes continue and the capillary pore system is shut down by hydration products (Maage et al., 1996). An alternative mechanism was proposed by him and his colleagues and this will be detailed in section 2.5, Age Effects and Ageing Factor.

2.3 CHLORIDE BINDING

The numerous reviews on chloride binding over the years show just how important the understanding of this phenomenon is, especially in terms of obtaining a fundamental diffusion value that is useful in service life modelling of concrete structures in chloride environment (Arya and Newman, 1990, Justnes, 1998, Siegwart et al., 2003, Glasser et al., 2008, Yuan et al., 2009). This short review on chloride binding will summarise what is known and highlight what Yuan et al., (2009) had left out or missed.

Some of the chloride ions that make their way into concrete are captured by a physical and chemical process called chloride binding. In general binding occurs as part of the diffusing chloride reacts chemically with the hydrating cement matrix forming Friedel's salt - $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$, or physically with the adsorption of chloride ion to the C–S–H phase of the concrete. Friedel's salt is a complex calcium chloroaluminate hydrate compound that forms as C_3A or C_4AF combines with chlorides that diffuses through the concrete or chlorides added in the mix (Mehta, 1991, St. John et al., 1998, Brown and Bothe Jr, 2004).

It is known that the binding reaction occurs rapidly in solute sodium chloride (NaCl) environment (Glasser et al., 2005). Geiker et al., (2007) supported this argument through an experimental programme using 25 year old cement paste. There are 2 mechanisms for the formation of Friedel's salt (Suryavanshi et al., 1996). The first mechanism proposed is the conversion of hydroxyl-AFm to Friedel's salt by ion exchange. The second mechanism is the absorption of Chloride ion (Cl^-) as Friedel's salt is formed by precipitation. They also proposed that both mechanisms work concurrently. In a study by Jones et al., (2003) using Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectroscopy, they proposed that the ion exchange mechanism is actually more dominant at an early age, with the precipitation mechanism gaining dominance at a later age.

2.3.1 Effect of cement types

It is known that fly ash, ggbs and metakaolin have a naturally high C_3A content and it has been shown that concrete with these constituents have low diffusion coefficient as a result of their binding capacity (Dhir and Jones, 1999, Dhir et al., 1996a, Glass and Buenfeld, 2000, Dhir et al., 2004). Figure 2.3 shows the effect of intrinsic permeability, chloride binding capacity and strength on chloride diffusion coefficient at varying fly ash replacement levels. It has been reported that optimum replacement level for fly ash is 30%,` with reduced binding capacity at 50% replacement (Dhir et al., 1997).

With ggbs, replacement levels of up to 70% results in better chloride binding (Mohammed et al., 2002a). Earlier, Dhir et al., (1996a) has shown the effect of ggbs on the intrinsic permeability and chloride binding capacity on chloride diffusion coefficient at several replacement levels up to 70% (see Figure 2.4). Silica fume concrete, although having a low binding capacity (Justnes, 1998), blocks the ingress of chlorides with a much improved particle packing. At a similar strength level, fly ash, ggbs and metakaolin concretes are better at resisting chloride ingress. Blending PC with either fly ash, ggbs or metakaolin cements increases the ratio of monosulphate to AFt, as monosulphate is the important precursor phase thereby increasing the potential binding sites (Jones et al., 2003).

Geiker et al., (2007) in their investigation found that the content of alkali metal ions (K_2O and Na_2O) has an important role to play in the distribution of chlorides between the pore solution, AFm solid solution and C-S-H.

2.3.2 Chloride binding isotherms

All four chloride binding isotherms, which describe the relationship between free and bound chloride ion over a given range of temperature cannot accurately predict the relationship within the complete concentration range normally experienced in practice. The Freundlich isotherm that has to be noted as fitting the chloride concentration of seawater, underestimated the relationship when binding is considered linear (Tang and Nilsson, 1993). Linear binding is seen in long term seawater exposure (Sandberg, 1999, Mohammed and Hamada, 2003). Sandberg's data obtained by a mixture of profile grinding and pore expression method suggested that for field concrete, the diffusion of chloride ions are affected by the counter diffusion of hydroxyl ions. He argued that in thin specimen laboratory experiments used to describe binding isotherms, the rate of removal of hydroxyl ions is faster, giving the impression of non-linear binding.

Mohammed and Hamada showing similar results collected from data on a range of cement/addition combinations including fly ash and ggbs with the age range of 10 to 30 years. While Sandberg (1999) suggested this could be due to the counter diffusion of hydroxyl ions, Xu (1997) considers that this happens as sulfate ions compete with chloride ions for binding sites. BET and Langmuir isotherm failed to express the relationship at higher concentrations (Yuan et al., 2009).

Thus, while the non-linear binding isotherm may work in an almost exclusively chloride environment such as the de-icing salt situation, result from Sandberg (1999) and Mohamed et al., (2002a) implies that they may not hold in a multi-ionic seawater situation.

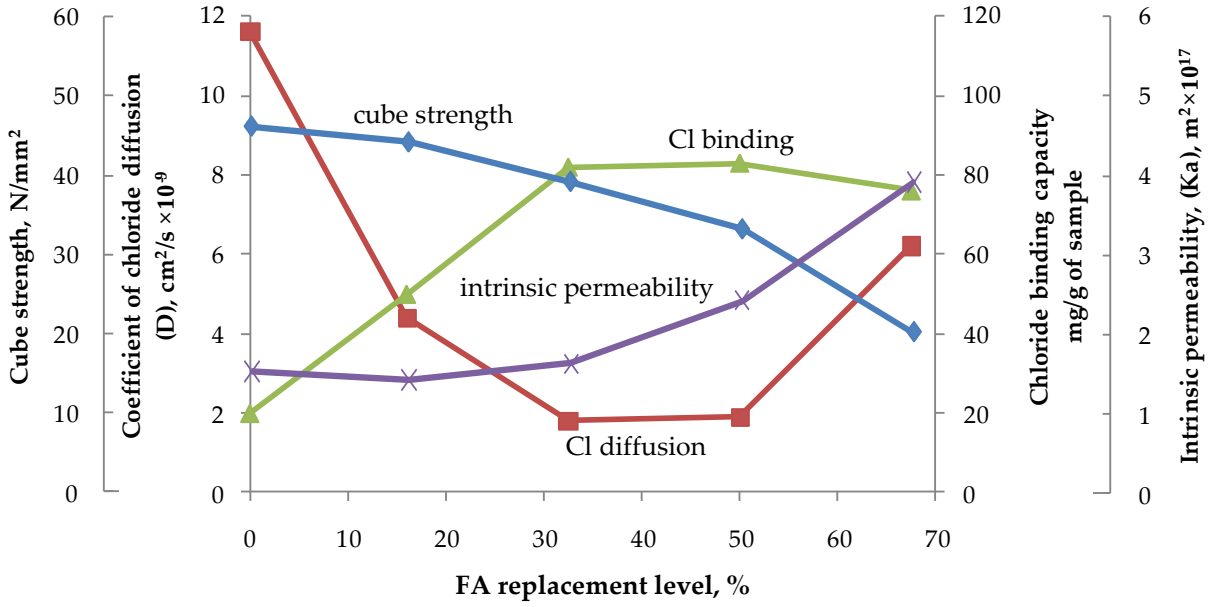


Figure 2.3 **Strength, coefficient of chloride diffusion, chloride binding capacity and intrinsic permeability of fly ash concrete (Dhir et al., 1997)**

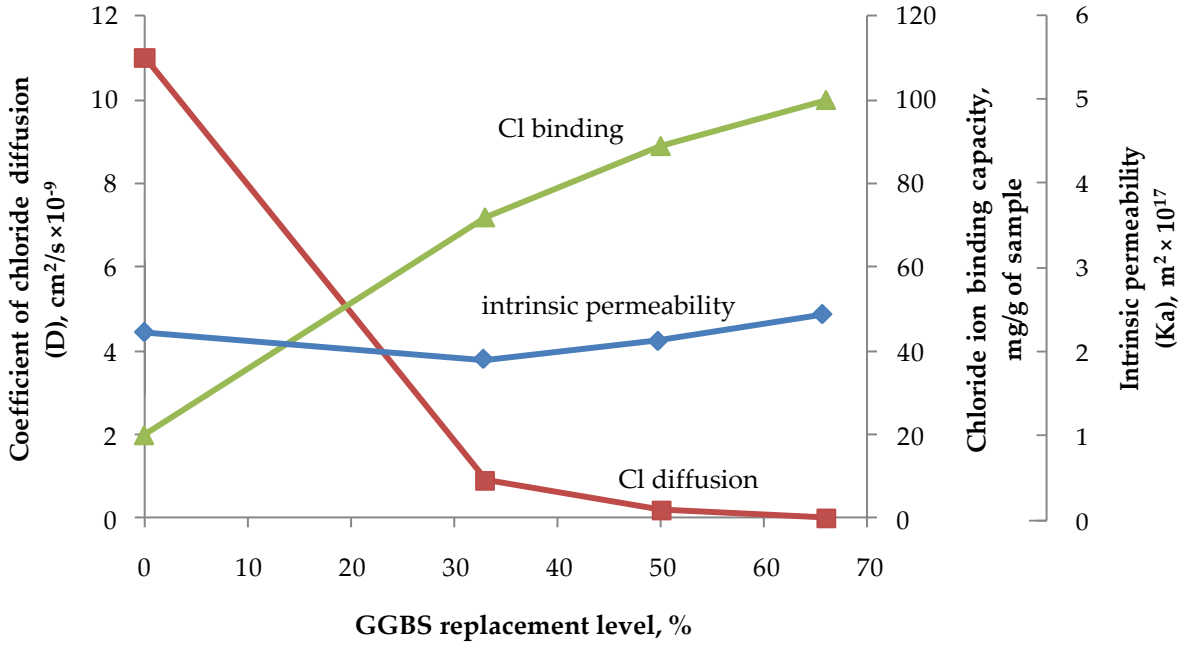


Figure 2.4 **Coefficient of chloride diffusion, chloride binding capacity and intrinsic permeability of ggbs concrete (Dhir et al., 1996a)**

2.3.3 Transport of chloride in a binding environment

Geiker et al., (2007) has reported through modelling and validation with independent published literature that binding occurs instantaneously. Using their phase equilibria model, it is suggested that cements with low alkali metal content would be the most effective in resisting chloride ingress as it is the content of alkali that governs the distribution of chloride between the AF_m solid phase, C-S-H and the pore solution.

The effect of binding on chloride transport is two-fold. Chloride binding effectively removes chloride from the transport processes and alters the concentration gradient that drives diffusion of chloride into the concrete (Glass and Buenfeld, 2000). The efficiency of chloride binding is determined by the amount of C_3A of the cement that combines with chlorides forming Friedel's salt (Glass and Buenfeld, 2000, Siegwart et al., 2003, Yuan et al., 2009). Chloride binding therefore, reduces the free chloride concentration that can diffuse through inside the concrete.

Dissolution of Friedel's salt can occur when the pH of the pore system drops below 12.5 and results from Glass et al., (2000) show that at pH 11.5 only roughly 2% of acid soluble chloride remained bound. This goes to suggest as carbonation progresses and the pH of the pore fluid falls, bound chloride is being released back again into the system allowing its participation in the corrosion process.

The Cl^-/OH^- ratio was thought to be important because the concentration of free chloride ion in the pore system alone does not provide sufficient indication of corrosion risk (Kayyali and Haque, 1995). The hydroxyl ion concentration indicates the ability of the pore solution to maintain high pH value to sustain repassivation of the steel reinforcement. Ann and Song, (2007) argue that the free chloride approach to Cl^-/OH^- ratio is flawed in light of the evidence that bound chloride does participate in sustained corrosion. They went on to suggest, based on work by Sergi and Glass, (2000) that the buffering capacity of cement matrix (i.e. the concentration of acid required to lower the pH of the pore solution) results in higher than the nominal chloride threshold level (> 0.40% by weight of cement) before corrosion could take place.

It is clear that concrete with high binding capacity can delay the onset of reinforcement corrosion. However, the binding phenomenon is still being resolved by the research community in order to give a more meaningful input towards service life modelling.

2.4 MARINE EXPOSED CONCRETE: PORE BLOCKING SKIN EFFECT

As stated earlier in Section 2.1.1, the surface of the concrete is quite different from the bulk of the concrete. Magnesium salts in marine environment, e.g. magnesium chloride ($MgCl_2$) and magnesium sulfate ($MgSO_4$), react with the calcium hydroxide forming brucite ($Mg(OH)_2$) and in the case of ($MgSO_4$) brucite and gypsum ($CaSO_4 \cdot 2H_2O$) (Černy and Rovnanìkovà, 2002). The formation of brucite skin on the paste rich layer have been suggested as providing a protective layer that could possibly block chloride ingress into the concrete (Buenfeld and Newman, 1986, Marshall, 1990, Mehta, 1991, St. John et al., 1998, Brown et al., 2003, Santhanam et al., 2006). Typical sea water contains 3200 ppm $MgCl_2$ and 2200 ppm $MgSO_4$ (Marshall, 1990). Typical reactions of both magnesium salts include:

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4 \cdot 2H_2O$$

$$MgSO_4 + [Ca(OH)_2 + 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 18H_2O] \rightarrow Mg(OH)_2 + 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$$

$$MgSO_4 + [Ca(OH)_2 + 3CaO \cdot 2SiO_2 \cdot 3H_2O] \rightarrow 4MgO \cdot SiO_2 \cdot 8H_2O + CaSO_4 \cdot 2H_2O$$

Helland (2008) recorded that diffusion coefficient decreases faster in saline solution than in fresh water. This is expected in a fresh and saline water comparison, because of Magnesium and Potassium exchange reactions with Calcium from concrete do not occur in fresh water.

When quoting Mohammed et al., (2002a) Helland concluded that the pore blocking effect had in-fact contributed to reduced chloride ingress. This is generally true, but is not the case for all cement types in sea water because Mohammed et al.'s work reveals that even though ion exchange did cause brucite formation up to 15 mm from the surface of the specimen, chloride still penetrates the specimens at a faster rate in the Portland and fly ash concretes in which brucite formed compared to the slag concretes where brucite was not detected. It seems that although there were pore blocking effects observed, they were not significant. This finding is in agreement with another earlier experiment (Jensen and Pratt, 1989). Comparing the strength between the mixes shows there is no correlation between different mix types on *D* values.

The SINTEF study used 8% SF in their mixes with very low water/cement ratio (0.36) (Helland, 2008) resulting in a very dense concrete (mean compressive strength = 77.5 N/mm^2). That could be why despite similar resistance to chloride ingress, ion exchange was not significant. Their concrete was denser and less permeable.

From another related paper published in the same year (Mohammed et al., 2002b) it was shown through SEM-EPMA (scanning electron microscope-electron probe micro analysis) that slag concrete exhibits denser morphology of C-S-H where it exhibits a more effective pore blocking effect than that of $Mg(OH)_2$ precipitation.

Investigation into a deteriorated concrete foundation of a harbour wall steps in South Wales (Sibbick et al., 2003) shows brucite formation in an eight year old carbonated structure. Although not tested for diffusion, it evidenced brucite formation in the outer surface as well as within microcracks, suggesting self healing of cracks by brucite formation. The thickness of the affected layer was approximately 100 μm–200 μm. Calcite was detected together with brucite in all instances.

In another publication (St. John et al., 1998), it was stated that wave impact and physical action of suspended abrasive particles can destroy the protective surface layer of brucite and aragonite ($CaCO_3$) which forms in contact with seawater. However, chloride ingress was stressed as the principle factor in concrete deterioration. As brucite is chemically almost insoluble in sea water (1.8 mg in 100gm of water at 20 °C (Černy and Rovnanìkovà, 2002)), the destruction of the protective layer may be implied to physical action or it may be argued in shallower water where fine particles are more likely to be in suspension allowing abrasion to the concrete skin. Incidentally this is where usually marine structures are constructed.

St. John et al., (1998) reiterated that permeability is said to be the most important factor in resisting chemical attack in sea water. Dense impermeable concrete is most resistant and this was in agreement with the result in (Mohammed et al., 2002b). The specific link between concrete permeability and chloride diffusivity has long been established through the work of Bentz, (Halamickova et al., 1995) and Buenfeld, (Ngala et al., 1995) that consistently shows as the concrete pore system becomes restricted through continuing hydration, chloride diffusivity reduces.

Mehta stated that apart from brucite, soluble products such as $CaCl_2$ and gypsum were also precipitated as a result of chemical reaction between salt and sea water (Mehta, 1991). Buenfeld and Newman, (1986) and Neville, (1995) reported that brucite formation is self limiting but forms rapidly. In Buenfeld's experiment on CEM I mortar immersed in seawater, 10 to 20 μm thick brucite developed in 24 hours and by four days attained maximum thickness of 35 μm. Consequently it cannot get thicker over time. However, it was reported in Mohammed et al., (2002b) to be precipitated deep in the surface zone. It could be that the CEM I and FA mix of the experiment was porous enough due to leaching of Portlandite to allow this deep penetration.

In another mortar study (Santhanam et al., 2006), it was found that brucite formation coexist with the consumption of calcium hydroxide (CH) and remains stable after the latter has been fully consumed. The 100 μm brucite layer was reported to offer better protection from sea water ingress although chloride ion Cl^- still diffuse into the concrete, evidenced by the low expansive nature of the ettringite formed.

Buenfeld and Newman (1986) suggested brucite precipitation is influenced by the pH of the seawater. Figure 2.5 shows that brucite is under-saturated by at least two orders of magnitude over the normal pH of sea water of 7.8 to 8.3. This means that as long as there is potential for reaction brucite will form continuously. They found that the typical brucite thickness formed is 25 μm after 130 days with a layer of aragonite that forms an outer skin on top of brucite. Although brucite is said to be relatively insoluble, Buenfeld suggested that the age profile would not be different because chlorides have entered the concrete before the permeability reduced.

For de-icing chemicals, brucite skin forms when $MgCl_2$ type de-icing salts are used. Sutter et al., (2006) found brucite on specimens exposed to 15% $MgCl_2$ for sorptivity test. However, in a comprehensive review to the US Portland Cement Association (Kozikowski et al., 2007), it was reported that brucite precipitation could actually be one of the mechanism for deterioration in weakened highway structures because of its mildly expansive nature.

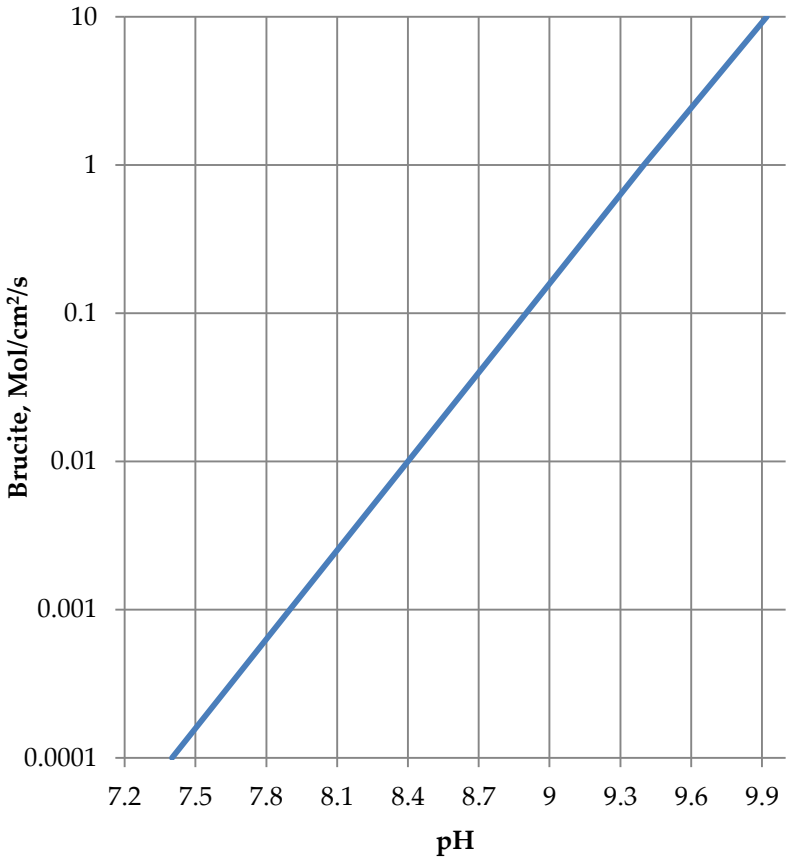


Figure 2.5 **The degree of saturation of sea water with respect to brucite, as a function of pH (Buenfeld and Newman, 1986)**

2.5 AGE EFFECTS AND AGEING FACTOR

Chloride diffusion models have been around for some time. A model proposed by Mario Collepardi based on the Fick's second law of diffusion in the 1970's was found to be too conservative (Helland, 2008). He and a group of others had earlier proposed another model based on his findings that show that there is a log-log relationship between chloride diffusion coefficient and age of maturity. This follows a straight line slope and they suggested the expression (Maage et al., 1996, Helland, 2008):

$$\boldsymbol{D_a(t) = D_{aO}\left(\frac{t_O}{t}\right)^{\alpha}} \qquad \textbf{Equation 2.9}$$

Where:

$D_a(t)$ = time dependent chloride diffusion coefficient

t = maturity age of the concrete

t_0 = reference maturity age typical of the concrete, normally at the age when the concrete is exposed for the first time

D_{a0} = achieved (apparent) chloride diffusion coefficient at the maturity age t_0, and

α = the ageing factor indicating the decrease of the apparent D (D_o) over time due to continued hydration and also binding effects.

A comprehensive guide was published by The Concrete Society (Bamforth, 2004), based on a model similar to this that attempts to model the behaviour and proposed ageing factors for different types of concrete. He detailed a modelling approach for durability using data from various sources. Bamforth's model takes the form :

$$\boldsymbol{C_x = C_s\left(1 - erf\frac{x}{2\sqrt{D_{ca(t_m)}\left(\frac{t}{t_m}\right)^{n} t}}\right)} \qquad \textbf{Equation 2.10}$$

where,

C_x = the chloride content at depth x at time t, in metres and seconds respectively

C_s = the surface level of chloride

$D_{ca(t_m)}$ = the apparent diffusion coefficient (m^2/s)at time t_m, in seconds

n = the age factor

Equation 2.10 above is obtained by substituting Equation 2.9 with the term D apparent in Collepardi's equation (introduced later in Section 2.8.1 as Equation 2.16). This report has also suggested typical ageing factors, i.e. the n value for several cements e.g. PC = -0.264, fly ash = -0.699

and blastfurnace slag = -0.621. The closer the age factor (n) is to 1, indicates better concrete. However, with regards to the proposed model, the ageing factors were based on empirical values current at that time and would have to be adjusted regularly to take into account the changes to the properties of cementing materials that happen in the future. Data used to base the ageing factors have a considerable spread although some does show clear relationship between the parameters in question. Bamforth reveals that they are taken generally not taking into account different circumstances of mix composition, water/cement ratio and exposure conditions that may well influence diffusion resistance of different concretes.

In a Pan-European approach, there are numerous models that are available to the concrete designer. A key model that is being used today is the International Federation for Structural Concrete (*fib*) model code, originated by the TG5 (fib, 2006). Another popular model is the Duracrete model (Bertolini, 2004). The problem with wide area models such as these is that they average out particular factors that tend to be specific to a region. Cement and aggregate's physical and chemical composition and production technique, for example, may be region specific producing different durability potentials. Similarly, models would have to be adjusted to take into account the changes to properties with novel materials. This fact was illustrated by Bamforth, (2004) in Figure 2.6 where modern Portland cement (CEM I) shows a different ageing factor from its older equivalent.

Specifying concrete based on a different range of materials by fitting it to a generic model would seem too simplistic as these models are largely complex. Given that concrete's interaction with its environment is more complex than what the models could predict, a practical approach is needed by concrete designers to take into account local knowledge of material performance while pursuing a probabilistic treatment of durability. In this respect, performance based specification may allow greater flexibility in design whereby durability is based on the actual material's performance rather than prescribed limiting value of current specification. It is therefore sensible to continue with the equivalent durability concept (to be described later in Section 2.9) to allow region specific referencing of concrete to take place and at the same time this could contribute towards refining the chloride ingress models.

2.5.1 Pore Structure: time/porosity/diffusion effects

Central to the debate of age effects in concrete and their potential in reducing chloride diffusion coefficient is the continual hydration of concrete over time. Chloride diffusion takes place in the capillary pore system and, as concrete matures, the pore system tightens and the width of the pore

decreases (Maage et al., 1996). It is known that dense concrete generally is better in resisting chloride ion penetration (Andrade et al., 1999).

Specific correlations between parameters that influence density, i.e. water-cement ratio and compressive strength, were made and it can be seen from the literature that lower water-cement ratio and higher compressive strength result in lower diffusion (Collepardi and Biagini, 1989, Dhir and Jones, 1999, Thomas and Matthews, 2004, Chalee et al., 2007). These correlations were based on natural diffusion or chloride profiling methods.

The effect of water-cement ratio and compressive strength complements the binding potential of different cements (Dhir et al., 1996b, Nokken et al., 2006b, Castellote et al., 2006). This causes the correlation to be ambiguous, especially when comparing different cement types at a similar water-cement ratio. However, compressive strength alone is not sufficient to describe or measure durability due to the binding effect of different cements (Baroghel-Bouny et al., 2007a).

Work done by Mejía et al., (2003) has shown that the diffusion coefficient decreases as porosity decreases for silica fume mortar. They suggested that the silica fume grain particles packed in between the cement particles thus lowering porosity and chloride diffusion. Another work (Ramezanianpour and Malhotra, 1995), done on different cements confirms that higher porosity results in more permeable concrete. This finding is again repeated in a recent work by Moon et al., (2006) showing better resistance from chloride penetration at increasing slag replacement level. Best performance was offered by a ternary blend of slag and fly ash. This last paper established a good correlation between pore structure and D_{nss} values for the type of cement tested. Chloride diffusion coefficient was determined using a modified NTBuild 492 test method and pore size measurement done with mercury intrusion porosimetry (MIP).

It should be noted that pore measurement using MIP have been found to be problematic (Abell et al., 1999). This is because of the debate on the MIP method (Diamond, 2000, Chatterji, 2001, Wild, 2001, Diamond, 2001a, Diamond, 2001b) as illustrated in Figure 2.7 where the 'ink bottle' effect causes overestimated fine capillary pore volumes and underestimated coarse capillary pores when the Washburn equation is applied. The equation is based on the model of a porous system with interconnected cylindrical pores that are accessible to the intrusion of mercury at subsequent pressure steps:

$$\boldsymbol{d = -4g\cos\theta / P} \qquad \textbf{Equation 2.11}$$

where d is the diameter of the cylinder being intruded, g is the surface tension of mercury, θ is the contact angle of mercury on the solid, and P is the applied pressure.

Diamond had suggested that the pore system of a concrete fails to conform to the requirement of the Washburn model. Nevertheless there is an agreement in the proposition that interpretation of MIP is still a good technique in comparing pore refinement at different stages of hydration (Wild, 2001).

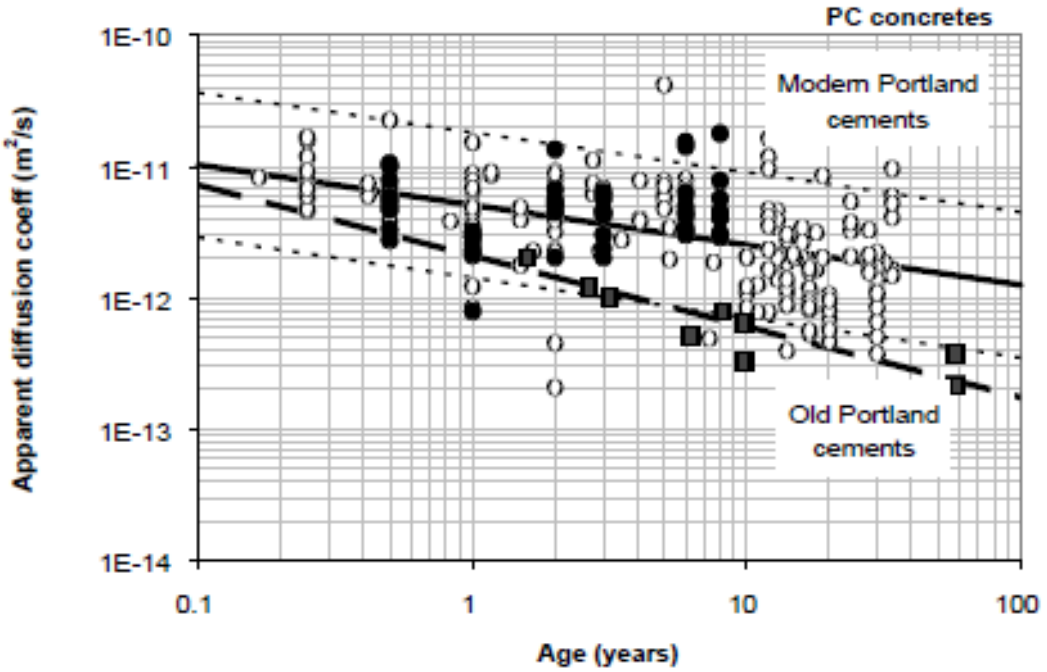


Figure 2.6 **Age dependant values for PC (Bamforth, 1996)**

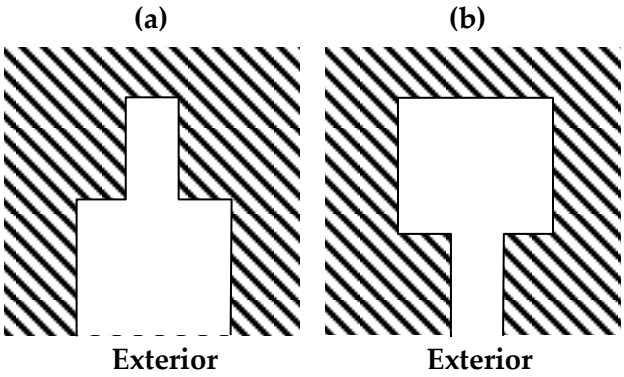


Figure 2.7 **Ink bottle effect that causes error in pore diameter calculation for MIP (Diamond, 2000)**

2.6 TEST METHODS FOR CHLORIDE RESISTANCE

The current EN-206 standard allows European member countries to have national provisions with respect to performance-based test method and performance-based specification. Currently there are two popular types of chloride resistance test methods in use within individual member countries and ASTM user countries. These are a), migration test where chloride ions are migrated through concrete specimens by applying an electrical field or b), diffusion test where chloride ions are allowed to diffuse to a predetermined period.

2.7 MIGRATION TEST

Chloride migration tests have been developed to establish chloride resistance of concrete in the shortest possible time. The advantage of speed enables rapid changes to concrete specification based on the comparison to a reference concrete. Since the 1980's a rapid test for chloride diffusion has been made available by the standardisation of a test method by Whiting (1981) (AASHTO, 1989, ASTM, 1997) although there are critical questions on the application of this test method, one being that this test measures total ion movement and not chloride ion movement alone.

Several researchers then proposed what are called as 'migration type tests', which are based on the two-cell test principles. Among others are the tests proposed by Dhir et al., (1990b), Tang and Nilsson, (Tang and Nilsson, 1992, Nordtest, 1995), Andrade et al., (Andrade, 1993, Andrade et al., 1994, Castellote et al., 2001b) and others (Truc et al., 2000, Prince and Gagné, 2001, Stanish et al., 2004b, Stanish et al., 2004a, Friedmann et al., 2004, Basheer et al., 2005, Sharfuddin Ahmed et al., 2008).

Migration tests work by accelerating the movement of chloride ions through applying a potential difference across the concrete specimen. A two-cell arrangement is needed to perform this process that contains, usually, chloride as catholyte and distilled water as anolyte separated by concrete specimen in the middle. Figure 2.8 shows a typical two cell test set-up. Measurement of the depth of ingress chloride ions is made using a variety of ways. Colorimetric indicators are used as is the monitoring of the movement of chloride ion either directly by measuring the evolution of chloride concentration in the downstream compartment or indirectly by monitoring, for example, the charge passed after a period of time and the conductivity of the anolyte solution.

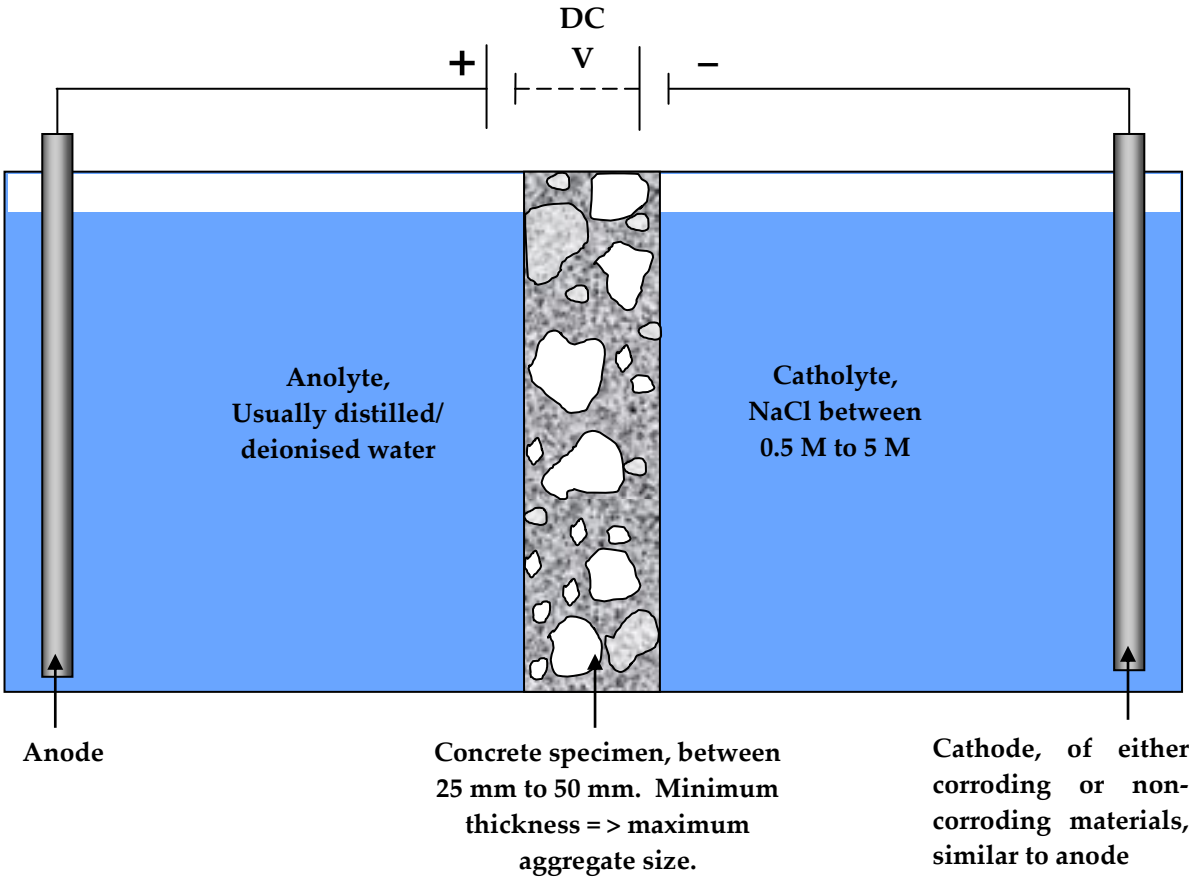


Figure 2.8 Typical two-cell rapid test setup

2.7.1 Theoretical foundation

2.7.1.1 Steady state migration

For steady state migration, modified Fick's First Law and Nernst-Planck equation were proposed by different researchers to obtain what they call a diffusion coefficient of a concrete specimen using a two-cell test. There are several reviews on the use of Fick's Law and Nernst-Planck equations with regards to the migration tests (Chatterji, 1997, Lu, 1997, Samson and Marchand, 1999, Samson et al., 2003, Krabbenhøft and Krabbenhøft, 2008). Firstly, diffusion of chloride into concrete can be described by Fick's First Law (Dhir et al., 1990b) as follows:

$$\boldsymbol{J = -D\frac{dC}{dx}} \qquad \textbf{Equation 2.12}$$

Under chemical and electrical potential, it is assumed that the flux of Cl^- is the sum of two processes namely diffusion and migration (Andrade, 1993, Tang, 1996). However, as the diffusion processed is being overwhelmed by migration in an electro-migration transport, the diffusion component of the equation is dropped due to it being negligible in favour of the migration component. Andrade then proposes a Nernst-Planck solution to the transport of Cl^- in a migration experiment.

A two-cell test setup is essentially a galvanic cell where the application of the Nernst-Planck equation is more suitable compared to the Fick's Law equation. The Nernst-Planck equation describes the flux of ions under the influence of concentration gradient and electrical charge through a diffusive membrane. It is now the most commonly used method. The use of this equation in a two-cell test was initially suggested by Andrade, (1993) as an alternative to the Rapid Chloride Penetration Test method (ASTM, 1997):

$$\boldsymbol{D_{ssm} = \frac{J_{Cl}\,RTl}{zFC_1\gamma\Delta\Phi}} \qquad \textbf{Equation 2.13}$$

where:

J_{Cl} = flux of chlorides (mol/cm^{2}s);

R = perfect gas constant (1.9872 cal/mol K);

T = average temperature during the test (K);

l = thickness of the sample (cm);

z = ion valence, for chloride, z = 1;

F = Faradays constant = 23060 (cal/ mol);

C_1 = Cl concentration in the catholyte (mol/cm^3);

γ = activity coefficient of the catholyte solution;

$\Delta\Phi$ = effective potential difference applied (V).

The flux of Cl^- is monitored using conductivity meter until a steady state flow is established. Figure 2.9 shows the schematic representation of the steady state test.

2.7.1.2 Non-steady state migration

For non-steady state migration, the Nernst-Planck approach is also being used for the standardised NT Build 492 in measuring the chloride migration coefficient albeit using a different solution:

$$D_{nssm} = \frac{RTL}{zFU} \cdot \frac{x_d - \alpha\sqrt{x_d}}{t} \qquad \textbf{Equation 2.14}$$

Where:

R = gas constant, R = 8.314 J/(K·mol);

T = average value of the initial and final temperatures in the anolyte solution, K;

L = thickness of the specimen, m;

z = value of ion valence, for chloride, z = 1;

F = Faraday constant, F = 9.648 ×10^4 J/(V·mol);

U = value of the applied potential difference, V;

x_d = average value of the penetration depths, m

α = lab constant; m;

t = test duration, s.

The profile for the theoretical solution of the NT Build 492 presents a problem where the sharp drop in the solution to the underlying equation (Tang and Nilsson, 1992) as seen in Figure 2.10 does not follow the experimental profile from migration experiments. Generally the profile follows a much smoother curve as observed in natural diffusion tests. Regardless, as a quality control procedure the chloride concentration detection corresponds to commonly accepted value of critical chloride concentration, hence making this test desirable as a quick test with a versatile application (Baroghel-Bouny et al., 2007a).

Castellote et al., (2001b, 2001c) proposed a 'time lag' concept to calculate the non-steady state migration in a two cell test. It is based on the intersection of the straight line steady state flux with the x-axis during the evolution of conductivity in the anolyte chamber during the test. The equation applied is:

$$\boldsymbol{D_{ns} = \frac{2l^2}{\tau v^2}\left[v coth \frac{v}{2} - 2\right]}$$ **Equation 2.15**

Where:

τ = time-lag in the migration test (s), from the start of the experiment to the x-axis intersection

l = thickness of the specimen (cm)

v = $ze(\Delta\phi)_t/k$T; where: k = Boltzmann's constant, T = average temperature during the test (K), $(\Delta\phi)_t$ = average effective voltage (V) through the specimen from the beginning until the time lag.

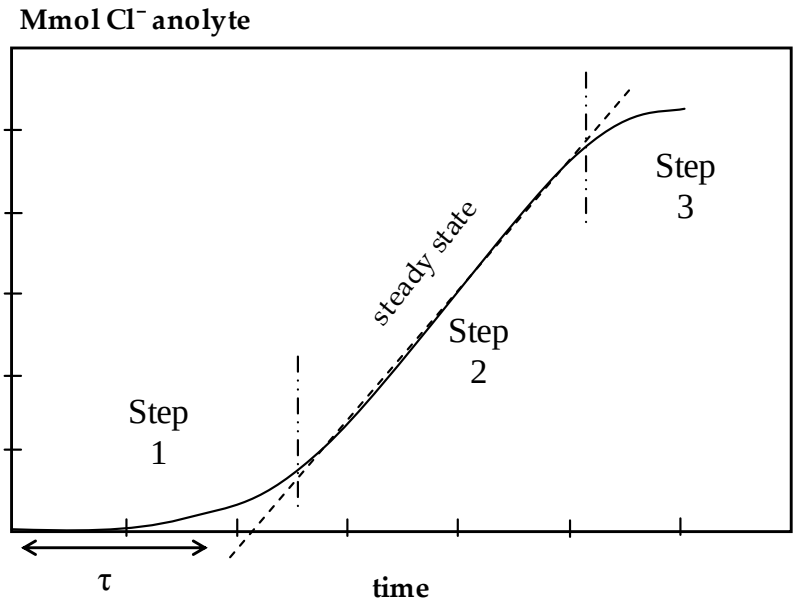


Figure 2.9 **Schematic representation of the evolution of conductivity and amount of chlorides in the anolyte during the test (Castellote et al., 1999)**

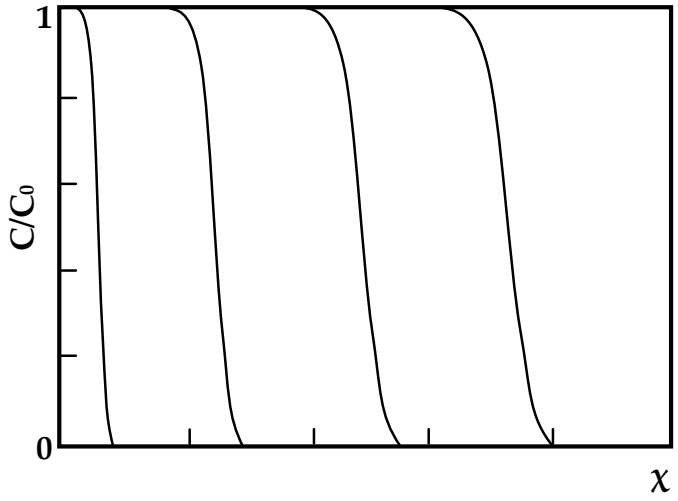


Figure 2.10 **Tsunami profile from the theoretical solution of the NT Build 492 test (Tang and Nilsson, 1992)**

2.7.2 Effects of cement type, cement content and water-cement ratio

A study by Dhir et al., (2004) shows that changes in cement content for CEM I does not bring about significant changes in steady-state D index measured by the PD method (Figure 2.11) although there is a clear upward trend observed with higher cement content. This finding is similar to another study by Persson, (2004), who did an extensive set of tests on self-compacting concrete and normal concrete using NT Build 492 method.

Dhir et al., (2004) found that the effect of water-cement ratio is more significant with lower water-cement ratios giving lower steady-state D index at similar cement content. This effect of water-cement ratio is repeated with binary cement mixes (CII/B-V and CIII/A) while the role of cement content becomes significant at higher water-cement ratio where the steady-state D index decreases with lower cement content (Figure 2.12).

The effects linked to variable water-cement ratio are also shown in a meta-analysis of several NT Build 492 studies; see Figure 2.13 and the data tabulation in APPENDIX B. For CEM I and fly ash cement concretes with water-cement ratio of more than 0.4, the diffusion coefficient is high, in some cases more than 20×10^{-12} m^2/s. For ggbs and silica fume cements, the diffusion coefficient is shown to be less than 1×10^{-13} m^2/s and this is similar across the whole range of water-cement ratios. However, it is inevitable that lower water-cement ratio concrete tends to have higher cement content thus masking the effect between high and low cement content.

Apart from water-cement ratio, cement types may be the most significant factor affecting the result of migration tests. At similar water-cement ratio, Dhir et al., (2004) shows that different cement types exhibits different steady-state D index values. Averaged index values reported in APPENDIX B by cement types are 19.4 for CEM I, 4.9 for fly ash, 3.7 for ggbs, and 2.2×10^{-12}m^2/s for silica fume respectively.

2.7.3 Effects of curing

Storage conditions, especially curing, have an effect on the concrete specimens used in the migration tests. It was reported that the measured resistance is higher with wet curing compared to other curing methods (Dhir et al., 1990b).

2.7.4 Effects of age at test

Ferreira et al., (2004) show that for migration testing using the NT Build 492 method, for specimens up to six months old , the measured diffusion coefficient reduces. At six months, D_{nssm} value is down to 1.05×10^{-12} m^2/s and 1.75×10^{-12} m^2/s for ggbs replacement levels of 70% and 53%

respectively from 6.65 × 10^{-12} m^2/s and 5.6 × 10^{-12} m^2/s at 28 days. As a comparison, D_{nssm} for fly ash cement reduces from 13 × 10^{-12} m^2/s to 3.5 × 10^{-12} m^2/s for the same period. Although the rate of reduction in value seems to favour fly ash, the difference between 1 × 10^{-12} m^2/s and 3.5 × 10^{-12} m^2/s is 250%, which is significant.

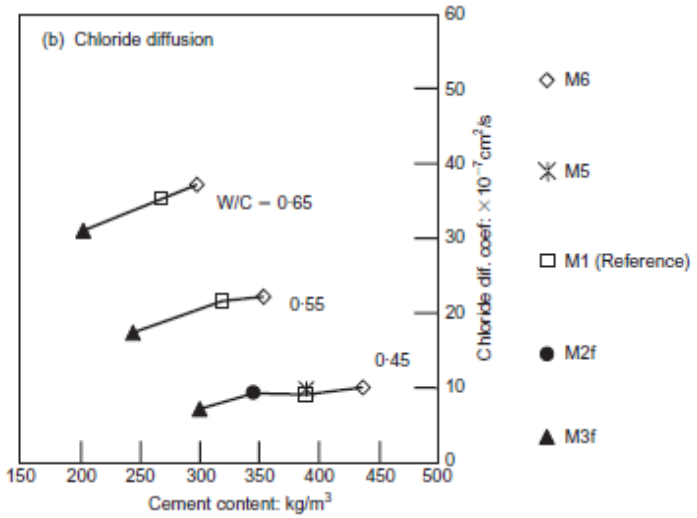


Figure 2.11 Influence of cement content on chloride diffusion index for CEM I (Dhir et al., 2004)

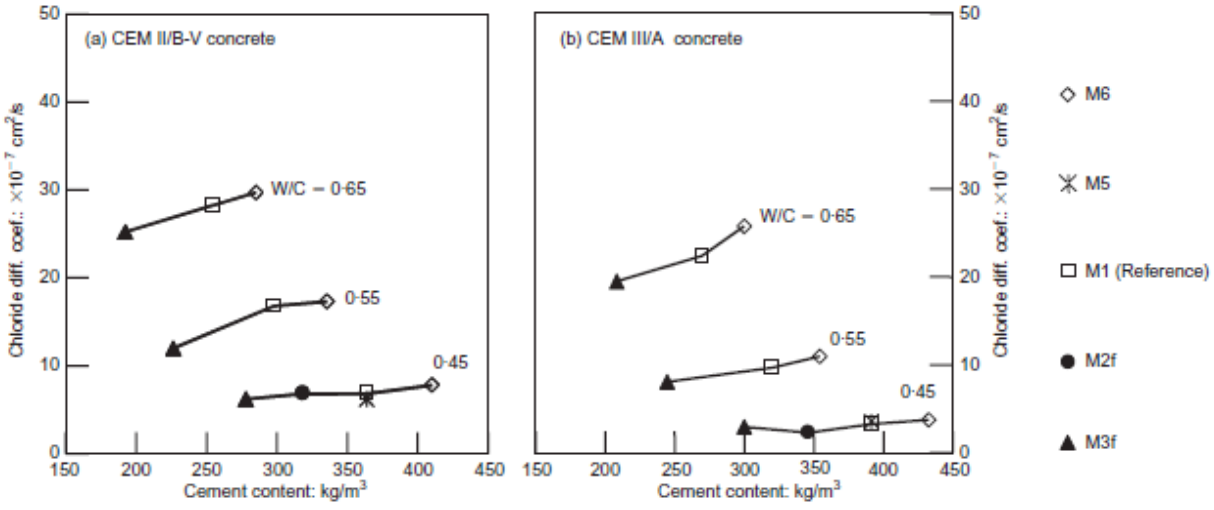


Figure 2.12 Influence of cement content on chloride diffusion index for CII/B-V and CIII/A [1] (Dhir et al., 2004)

[1] The test only calculates the diffusion index and not absolute diffusion, 1 × 10^{-7} cm^2/s = 1× 10^{-11} m^2/s.

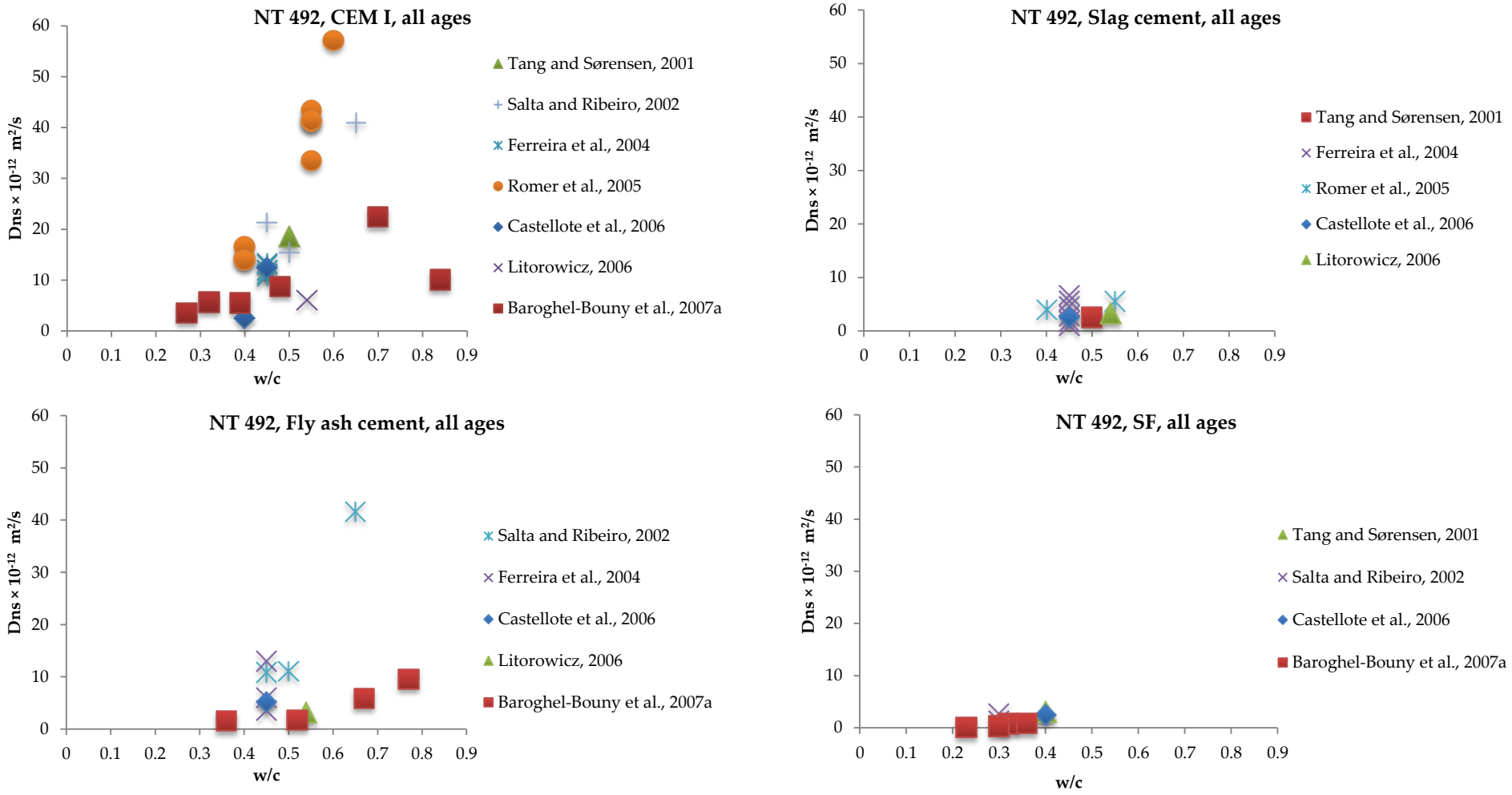


Figure 2.13 **Effect of w/c on NT Build 492 (a)-CEM I, (b) ggbs, (c) Fly ash, (d) silica fume**

2.7.5 Effects of solutions used for anolyte and catholyte

Various catholyte concentrations are used in the two-cell test methods, as reported in Table 2.2. The 3% NaCl was meant to be reflective of the approximate Cl^- concentration of seawater, calculated as 0.46 M. Concentrations of higher than 0.5 M are often used because it is suggested that chloride binding in the migration test using solution under 0.5 M is low and does not reflect binding in the natural diffusion test (Castellote et al., 2001b).

A study of the effect of polarisation on the migration test performed on Portland cement concrete shows that at 12 volt potential, the electrostatic field is not substantially distorted and led the authors to believe that migration experiments (Multi-Regime) can reliably estimate the diffusion coefficient (Castellote et al., 2001a). A value of 1 M was proposed to be appropriate by Andrade, (2002). This links with their view that the Nernst-Planck solution results in an absolute diffusion value. The counter argument suggests that as the ions are indeed polarised due to the application of potential difference, diffusion values obtained from migration experiment cannot be taken as representative of the diffusion coefficient.

A paper by Prince and Gagné (2001) reported that different upstream and downstream solutions have an effect on the two-cell migration test . Their experiment, using only CEM I concrete, shows that the change in electrolyte solution both anodic and cathodic affects the chloride flow and other ionic species, e.g. hydroxyl ions, from within the concrete specimen. This can have an effect on the conductivity measurement. They have also shown that hydroxyl ions (OH^-) concentration also affected the anodic potential where an increase in its concentration alters conductivity and causes an increase in the current intensity. They went on to suggest that in order to make comparison between tests, experimental conditions must be identical. This point has also been stated earlier (Andrade et al., 2000).

It is known that OH^- moves to either side of the cell in an electro-migration experiment. Additionally, thiosulfate ions in ggbs concrete (Gollop and Taylor, 1996, Roy, 2009) blocks electrical charge potentially giving false result with test methods that use any kind of electrical measurement, i.e. conductivity, coulombs or even ion selective electrode. Charge blocking capacity is high in thiosulfate as it commonly is used in electrical engineering as aqueous-electrolyte resistor (Beverly and Campbell, 1995).

2.7.6 Effects of other parameters

The Report from RILEM TC 116-PCD concluded that specimen preconditioning is sensitive to test methods (Andrade et al., 1999).

Applying potential difference forces ions to move faster within the upstream cell and the downstream cell, hence shorten the test period especially for the steady-state test. However, this causes specific perturbance to the specimen and accelerates the dissolution of the anode. Andrade, (1993) in her critique of the ASTM C1202 test method stated that at high voltage values, the temperature of the specimen rises causing changes in the velocity of the ion movement. Researchers have now settled on 10 V – 12 V as reasonable for steady-state tests in that it allows the test to run relatively quickly without too much perturbance to the specimen or the electrolyte movement. Higher voltage may also cause a faster degradation of the electrode, as seen in the PD method (Dhir et al., 1990b), or for non-corroding electrodes, the evolution of chlorine gas in the downstream section of the migration cell.

The non steady-state migration test NT Build 492 allows higher voltages from 30 V – 60 V depending on the resistivity of the specimen for the test as long as its temperature and that of the solution are maintained at 22 ±2 °C.

Ting (2003) and Price et al., (2003) did extensive work on aggregate effects using six different aggregate types with different water absorption ranging from 0.5% to 3.2% and shown that aggregates with high porosity allows more chloride ingress into the concrete. Ting's PhD work detailed the aggregate effects on the measurement of accelerated chloride diffusion index using the PD method, and demonstrated that aggregate effects are significant even at a fixed water-cement ratio. The aggregate with the least water absorption (0.5%) to the highest water absorption (3.2%) shows an increase in chloride penetration by approximately 180%. This is compared to 110% increase in chloride penetration when concretes made with the most absorptive aggregate (i.e. aggregate with water absorption of 3.2%) had the water-cement ratio reduced from 0.40 to 0.60.

He went on further to show that, at varying cement contents and a fixed water-cement ratio, aggregate influence was greater than the influence of cement content. The PD index increased 260% when the aggregate water absorption increased from 0.5% to 3.2%. However, for a single aggregate type, there was typically a 20% increase in the PD Index when the cement content was increased from 310 kg/m^3 to 445 kg/m^3 at a fixed water-cement of 0.45.

In the early days of the migration testing, specimen thickness was relatively thin, usually less than 10 mm. This was later found as inadequate because with such thin sections the aggregate-paste

interface may go completely through the section giving a preferential path for chloride movement (Dhir et al., 1991). Additionally porous aggregates have been found to be able to move Cl^- more rapidly than the paste fraction of the concrete. The minimum thickness adopted currently is 25 mm for 20 mm nominal size aggregates.

Persson, (2004) using NT Build 492 found that D_{nssm} decreases with increasing aggregate content and argues that chloride only passes in his case through the cement paste and the transition zone. The aggregate used in his study was crushed gneiss. Table 2.2 lists known migration test methods and highlights their similarities and differences.

Table 2.2 Migration type tests for chloride resistance

Test name	Reference	Specimen dimensions	Applied potential	Anolyte	Catholyte	Output of test	Repeatability, %	Reproducibility, %
ASTM C 1202-97	(ASTM, 1997)	Ø 100mm × 50mm	60 V	0.3 mol/L NaOH	3.0% NaCl (0.46 mol/L)	Permeability ranking	10	20
NT Build 492	(Nordtest, 1995)	Ø 100mm × 50mm	10 – 60 V	0.3 mol/L NaOH	10% NaCl (1.71 mol/L)	D_{ns}	18	36
Truc et al.	(Truc et al., 2000)	Ø 110mm × 30mm	12 V	NaOH (0.025 mol/L) + KOH (0.083 mol/L)	NaOH (0.025 mol/L) + KOH (0.083 mol/L + NaCl (0.564 mol/L)	D_s	19	77
Multi-regime method	(Castellote et al., 2001b)	Ø 75mm × 25mm	12 V	Distilled/ deionised water	1 mol/L NaCl	D_s/D_{ns}	22/25	69/49
Migration colouri-metric method	(Castellote et al., 2001c)	Ø 100mm × 150mm	12 V	Distilled water	0.5 mol/L NaCl	D_{ns}	29	40

Cont'd…

Table 2.2 cont'd…

Test name	Reference	Specimen dimensions	Applied potential	Anolyte	Catholyte	Output of test	Repeatability, %	Reproducibility, %
Potential difference	(Dhir et al., 1990b)	100mm Ø, 25mm	10 V	Distilled/ deionised water	5 mol/L NaCl	D_s (index)	COV 7.1%	Not reported
PERMIT	(Basheer et al., 2005)	insitu	60 V	Deionised water	0.55 mol/L NaCl	D_s (index)	Not reported	Not reported
UCT chloride conduction	(Sharfuddin Ahmed et al., 2008)	Ø 65mm × 25mm	10 V	5 mol/L NaCl	5 mol/L NaCl	mS/cm	Not reported	Not reported
Integral corrosion test	(Castellote et al., 2002)	70mm × 70mm cube + rebar	10 -12 V	Deionised water	1 mol/L NaCl	$D_{ns} + C_s + C_{crit} + I_{corr}$	Not reported	Not reported

2.8 NON STEADY-STATE DIFFUSION TESTS

CEN, through CEN/TC51/WG12/TG5 has confirmed the status of TS 12390-11 as a Technical Specification (TS). Its status as a Technical Specification (i.e. a draft for development) and not a full European standard was the result of not having precision data. Its publication was followed by a European round robin test conducted in 2010 where the University of Dundee was a participant. The test was designed based on several test methods since AASHTO T259 in 1980, ASTM C1543 and NT Build 443 which was standardised for the Nordic countries in 1995 (Tang et al., 2012).

Generally the test employs a cube or cylinder specimen exposed to uniaxial chloride ingress over a period of time. This is done by water tight coating of all but one side of the specimen and either immersing, ponding or inversion of the specimen in 3% by mass chloride solution. Figure 2.14 shows typical example of all three acceptable methods.

After 90 days of exposure, powder samples of the specimen are obtained by grinding a minimum of eight parallel layers from which acid soluble chloride content is determined. The chloride profile obtained is then used in a non-linear regression analysis excluding the first layer to fit the profile to the least squares method. Optimal fit of the regression analysis is determined using surface chloride concentration and the non steady-state diffusion coefficient as parameters.

2.8.1 Theoretical foundation

From Equation 2.4 in Section 0, the Fick's second law of diffusion is integrated under the assumption of: (1) the concentration of chloride ion at the surface is constant throughout, $C_s (C = C_s$ for $x = 0$ at any $t)$; (2) D does not vary in time and the concrete is homogeneous; (3) The specimen does not contain chloride initially: , $C = 0$ for $x > 0$ and $t = 0$. From this, the solution is often written since Collepardi in the 1970's as (Bamforth and Price, 1993, Costa and Appleton, 1999, Černy and Rovnanìkovà, 2002, Andrade, 2002, Broomfield, 2006, Song et al., 2008):

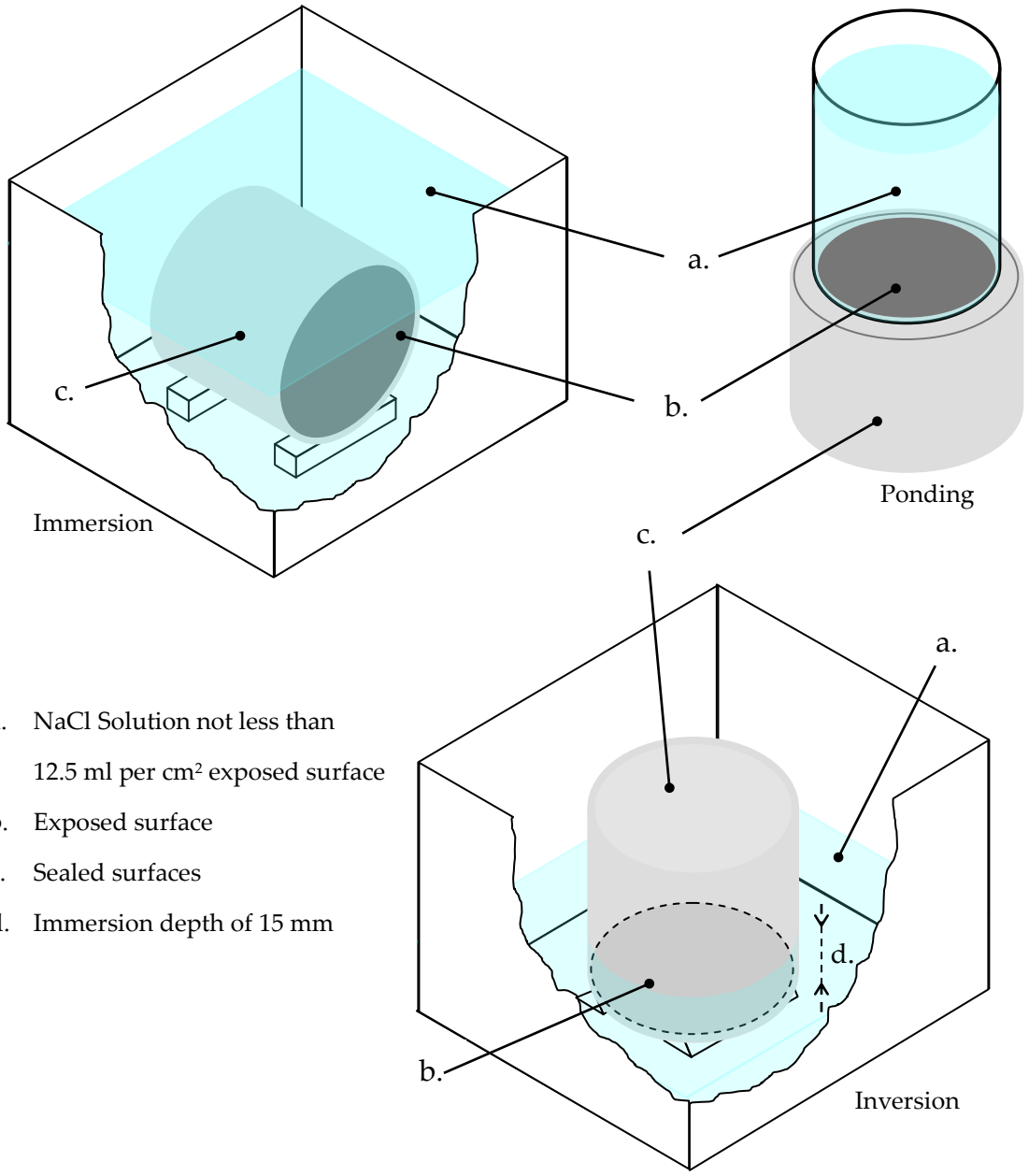
$$C_x = C_s \left(1 - erf \frac{x}{2\sqrt{D_{app} t}}\right) \qquad \textbf{Equation 2.16}$$

where

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-u^2)\, du \qquad \textbf{Equation 2.17}$$

In the CEN TS 12390-11:2010, the equation is written as:

$$C_x = C_i + (C_s - C_i) \left(1 - erf\left[\frac{x}{2\sqrt{D_{nss} t}}\right]\right) \qquad \textbf{Equation 2.18}$$



a. NaCl Solution not less than 12.5 ml per cm^2 exposed surface
b. Exposed surface
c. Sealed surfaces
d. Immersion depth of 15 mm

Figure 2.14 Schematic representation of three types of exposure for CEN TS 12390-11:2010

which is identical to NT Build 443:

$$\boldsymbol{C(x,t) = C_s - (C_s - C_i) \cdot erf\left(\frac{x}{\sqrt{4D_{app}t}}\right)} \qquad \textbf{Equation 2.19}$$

taking into account initial chloride concentration of the concrete if any, where

$C_x \equiv C(x,t)$ = chloride content measured at average depth x at exposure time t, % by mass of concrete

C_S = Calculated chloride content at the exposed surface, % by mass of concrete

C_i = Initial chloride content, % by mass of concrete

x = Depth below the exposed surface to the midpoint of the ground layer, m

D_{app} = Non steady-state diffusion coefficient, m²/s. Note that Equation 2.19 uses the term D_{app} (apparent diffusion coefficient). However, the term 'non steady-state' and 'apparent' mean the same and are interchangeable.

t = Exposure time, seconds

erf = Error function defined in equation 2.17

Bertolini et al. (2006), commented that the assumptions made to theoretically describe the kinetics of the apparent point-wise diffusion (D_{nss}) are rarely met in real structures. However, these factors can be controlled in an experimental setting, thus CEN TS 12390-11:2010 has been designed in such a way.

2.8.2 Acid soluble chloride

The determination of chloride content is made in accordance with EN 14629:2007, an acid soluble chloride extraction method.

In reality, acid soluble chloride does not represent the total chloride content of a sample. Dhir et al., (1990a) in a study into admixed chloride content in Portland cement concrete found that acid soluble method (in their case according to BS 1881:1988 Part 124) only accounts to about 80%-94% (mean variation of 12%) compared to total chloride content as measured by X-ray florescence spectroscopy (XRF) method. The difference between EN 14629:2007 and BS 1881:1988 Part 124 is the molarity of the nitric acid, which is 5 mol/L and 2.67 mol/L respectively. Table 2.3 shows the comparison between acid soluble chloride and total chloride as presented by Dhir et al.

Comparing the acid soluble and water soluble methods to extract chloride from solution, they concluded using acid extraction overestimates the risk of reinforcement corrosion as it is the free chloride that participates actively under normal circumstances. They went on to say that different extraction method causes different amount of chloride to be brought into solution suggesting sensitivity of this method to operator error. However, no published literature could be found that compares measurement of chloride content according to BS EN 14629:2007 method with total chloride content obtained with XRF.

2.8.3 Surface chloride (C_s) values

CEN TS 12390-11:2010 requires the first layer of chloride analysed to be excluded from the regression analysis. Indeed, a typical chloride profile from CEN TS 12390-11:2010 method shown in Figure 2.15 shows that the first layer or sometimes even deeper, the measured chloride does not fit the regression profile. This makes direct measurement unreliable. The C_s value is thus inferred by extrapolation of the regression curve of the chloride profile.

Equation 2.16 shows that the build up of chloride along the concentration gradient is controlled by D_{nss} and C_s. The surface chloride value is important, as it determines the baseline of the concentration gradient. More importantly, C_s value is one of the controlling parameter that affects the prediction used in service life modelling, the other being C_{crit} or critical/threshold chloride content.

In general, the composition of the first few millimetres of a concrete is different from the rest of the bulk concrete because of contact with formwork and segregation of aggregates near the surface (Andrade et al., 1995), during concrete casting. Poulsen and Mejlbro, (2006) reportedly found 'humps' in the chloride profiles typically derived from seawater exposure at a distance of 50% of the maximum aggregate size from the surface although they did not explain why this is the case. This difference in composition and the observed resulting profile of the surface chloride level is similarly influence by location and orientation of the surface, degree of salt exposure and general exposure conditions with regards to the prevailing wind (Bamforth and Price, 1993).

Cement composition (cement type, chloride binding capacity, absorption) also plays a part (Bertolini et al., 2006) in determining C_s. C_s was suggested to vary with time (Andrade, 2002) although Bertolini et al., (2006) reported that the value stabilises after one to two years. In an earlier study, it was observed that C_s value remains relatively stable up to three years (Bamforth and Price, 1993) and in another study, 10 months (Mangat and Molloy, 1994).

It has to be noted however, the variability of C_s on the surface layer does also appear in a laboratory setting where the concrete surface has been cut and the diffusing surface can be considered homogeneous throughout. It is suggested that the variability of C_s on the surface layer may be due to the micro-cracks that developed on the concrete surface as a result of cutting the specimens using diamond saw during preparation for the test. With respect to the test method, the effects of parameters other than location and exposure conditions will be explored here.

2.8.3.1 Effects of cement content

Bamforth and Price, (1993) reported that for marine structures, C_s values seems to increase with the increase in cement content. However, their data pool was scattered and by taking out one set of data the reported correlation diminished. In a meta-analysis of a completely different set of data, this time from 90 days tests in laboratory exposure conditions shows the same trend. That is, C_s values do not seem to increase with the increase in cement content, as shown in Figure 2.16. APPENDIX C summarises the published literature reviewed in Figure 2.16.

2.8.3.2 Effects of cement type

Song et al., (2008) reported that C_s is high in bended cements as a result of chloride binding. In a neural network study on factors influencing binding by Glass and Buenfeld, (2000), they found that when tricalcium aluminate (C_3A) content is high, C_s value is similarly high. They suggested that this is the result of concentrating effect due to the binding capacity although this also causes less free chloride to move further inwards reducing the depth of penetration.

Table 2.3 Comparison between acid soluble chloride content and XRF (Dhir et al., 1990a)

True Cl^- content (% weight cement content)		Measured Cl^- content			
		Measurement Technique			
		Volhard (BS 1881: Part 124)		XRF	
Low	0.10	0.08[A]	(80)[B]	0.09[A]	(97)[B]
	0.25	0.21	(84)	0.24	(98)
Medium	0.50	0.43	(86)	0.49	(98)
	0.75	0.65	(86)	0.72	(97)
	1.00	0.89	(89)	0.98	(98)
High	1.50	1.38	(92)	1.48	(99)
	2.00	1.88	(94)	2.02	(101)
Mean variation from true content			-12%		-2%

Note:
[A] % weight cement content
[B] (% of the true content)

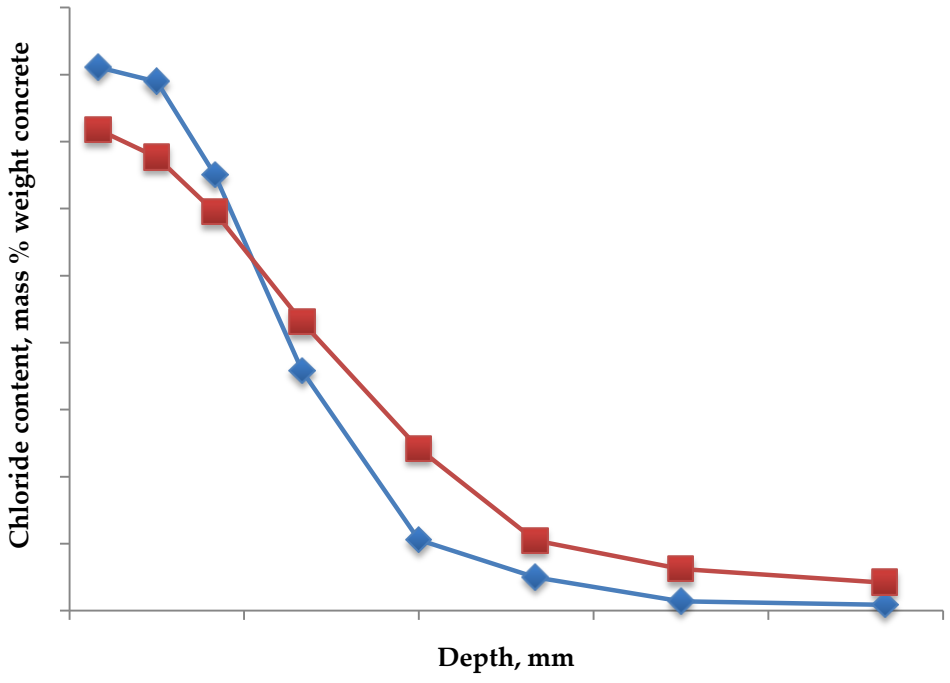


Figure 2.15 Typical chloride profile from analysis of powdered samples

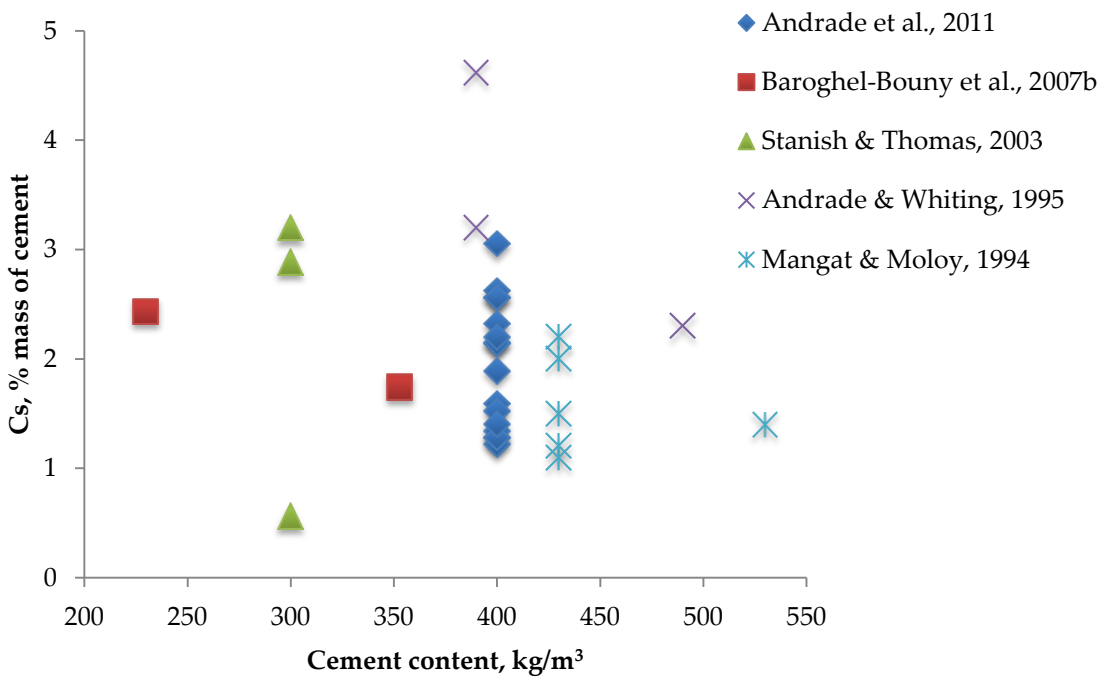


Figure 2.16 Effect of cement content on C_s with 90 days non-steady state laboratory tests

2.8.4 Non steady-state diffusion coefficient and the minimum D_{nss} achievable.

Commonly the purpose of the test method is to obtain the apparent or non steady-state diffusion coefficient of a concrete. This relates to the average rate at which chloride diffuses from the concrete surface towards the reinforcement steel inside the concrete at a specific period of time. D_{nss} values are heavily influenced by cement type (Bamforth and Price, 1993, Bertolini et al., 2006, Song et al., 2008). Bertolini et al. (2006) reported that factors which determine the pore structure of the concrete have a considerable effect, such as water-cement ratio, compaction, curing and the presence of microcracks.

The term D_{nss} from the CEN TS 12390-11:2010 equation can be determined by rearranging Equation 2.18. This showed that the equation in question has a natural exponential curve:

$$D_{nss} = \frac{x^2}{4t}\left(\frac{1}{erf^{-1}\left[1-\frac{C_x-C_i}{C_s-C_i}\right]}\right)^2 \qquad \textbf{Equation 2.20}$$

2.8.4.1 Effects of cement type

It has been generally known that concrete blended with fly ash and ggbs has a longer service life compared to Portland cement concrete (Bertolini et al., 2006). An example of the beneficial improvement by varying cement type can be seen in fly ash replacement as depicted in Table 2.4. Bamforth and Price (1993) commented, based on a review of several published results that using increasing amount of type II additions, namely fly ash, ggbs and silica fume further reduces the apparent diffusion coefficient values up to two orders of magnitude. This effect can also be seen from Blezinsky et al., (2002) with significant reduction of D_{nss} with increasing ggbs replacement levels. The average coefficient of diffusion for the whole data set in APPENDIX C separated by cement type is CEMI 16.4 × 10^{-12} m^2/s, fly ash 4.4 × 10^{-12} m^2/s, ggbs 2.0 × 10^{-12} m^2/s, and silica fume 4.0 × 10^{-12} m^2/s respectively.

Table 2.4 Effect of cement type on apparent diffusion coefficient values (Andrade et al., 2011)

Cement type	D_{nss}, × 10^{-12} m^2/s
CEMI	21.0
SF 9%	10.8
FA 35%	4.4
FA 35% - SF 9%	2.2

Note:
All concrete made with 400kg/m^3 total cement, 4 months age during test, 0.45 w/c except FA 35% - SF 9% @ 0.56 w/c

2.8.4.2 Effects of cement content

No single study that compares the effect of cement content on diffusion coefficient values using similar test methods can be found in any of the literature. However, another look at the compilation of data in APPENDIX C shows that there is no visible trend to the reported D_{nss} value as cement content increases (see Figure 2.17). It is important to note that in most cases, cement content and water-cement ratio are interdependent, i.e. cement content is used to change water-cement ratio where high cement content = low water-cement ratio shown in Figure 2.18. This is similar to the findings from the migration test reported in section 2.7 which show that the effect of cement content only became apparent at high water-cement ratio. These sets of data cover water-cement ratio from 0.32 to 0.58. The high values for D_{nss} observed in Andrade et al., (2001) covers increasing diffusion coefficient with increasing age for CEM I.

2.8.4.3 Effects of water-cement ratio

Part of the review on the effects of water-cement ratio have been covered in section 2.5.1. In general, for field structures there is a correlation especially for a log-linear plot between effective diffusion coefficient and water-cement ratio that shows lower diffusion coefficient with lower water-cement ratio (Hobbs, 1998). However, for the dataset explored, the correlation as seen in Figure 2.19 is not clear although it can be generally deduced that as water-cement ratio increases, diffusion coefficients reported are higher.

2.8.4.4 Effects of age at test

Data by Blezinsky et al., (2002) and Andrade et al., (2011) shows that as expected, diffusion coefficient reduces continually as concrete ages. However, the rates at which the diffusion coefficient reduces are different. Blezinsky et al.'s data shown in Figure 2.20 tested with

NT Build 443 shows mostly negligible reduction through 24 months ageing. His concrete was mainly 0.42 water-cement ratio.

However, Andrade et al.'s data tested with AASHTO T 259 showed significant ageing effect. For example, 35% fly ash 0.45 water-cement ratio mix reduced by almost 100% from 4.4×10^{-12} m^2/s to 0.58×10^{-12} m^2/s. Andrade et al.'s data also reveals a surprising result that shows CEM I performing erratically over the period of 36 months although no explanation was offered as to why this is the case.

In both experiment, ponding method was used and Fick's second law solution was applied. The only difference was the ponding period of 40 days and 90 days for Blezinsky et al., (2002) and Andrade et al., (2011) respectively.

2.8.4.5 Effects of other parameters

The data compilation also shows that the effect of contact solution concentration is not clear. No publication was found that explores other parameters that may affect the results of the test such as solution volume although the test method specifies a minimum allowed.

2.8.5 Sensitivity of the test method

The review of the published data shows that the sensitivity of the test method decreases with the decrease in water-cement ratio. Effects of cement content although still visible do not constitute a significant contribution to the advancement of the debate on the effect of cement content on the chloride diffusion coefficient because of the scatter of available data. However, with respect to real structures with largely low water-cement and high replacement content the difference between concretes it is still hard to establish. This could either be one of the following. 1) The resolution of available test methods are not sensitive enough to differentiate between these 'high performance' concrete or 2) At low diffusion coefficient values, the composition of the structural concrete has less importance in resistance to chloride ingress and other factors such as particle packing, cracks or microcracks and quality of workmanship are more important.

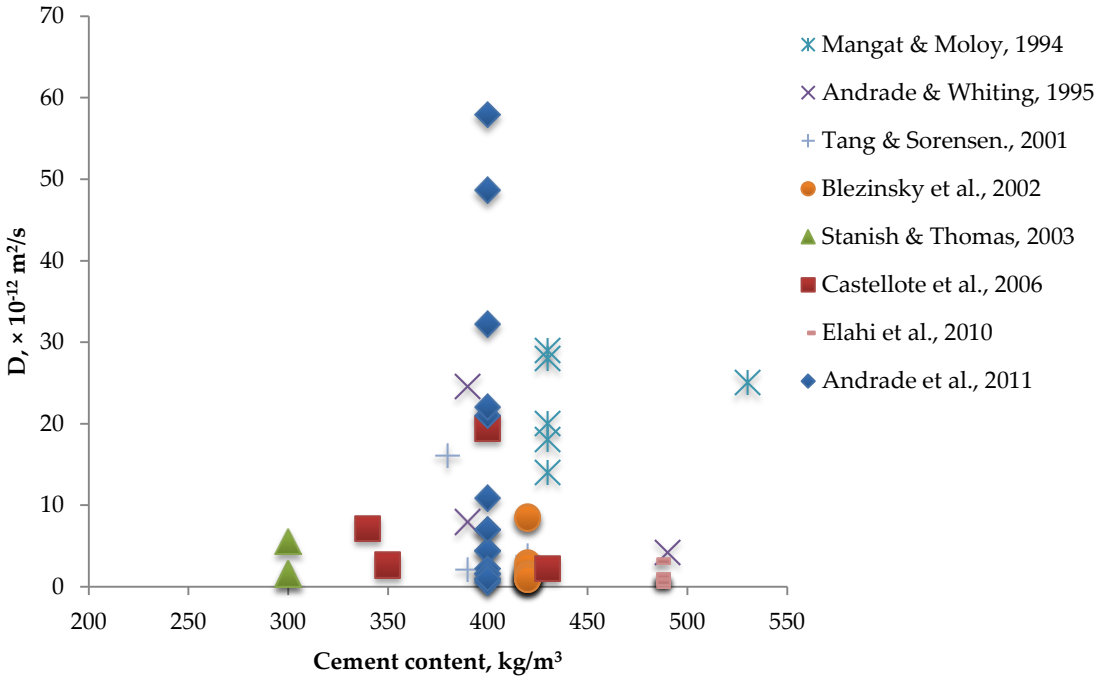


Figure 2.17 Relationship between D_{nss} and cement content

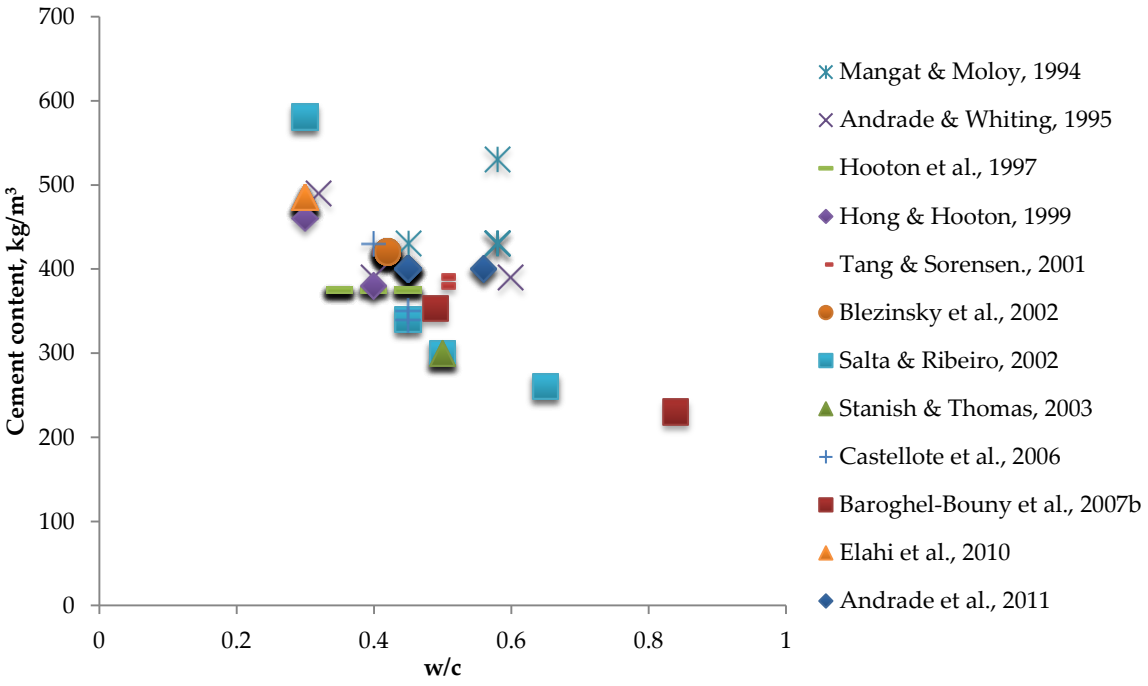


Figure 2.18 Relationship between cement content and water-cement ratio

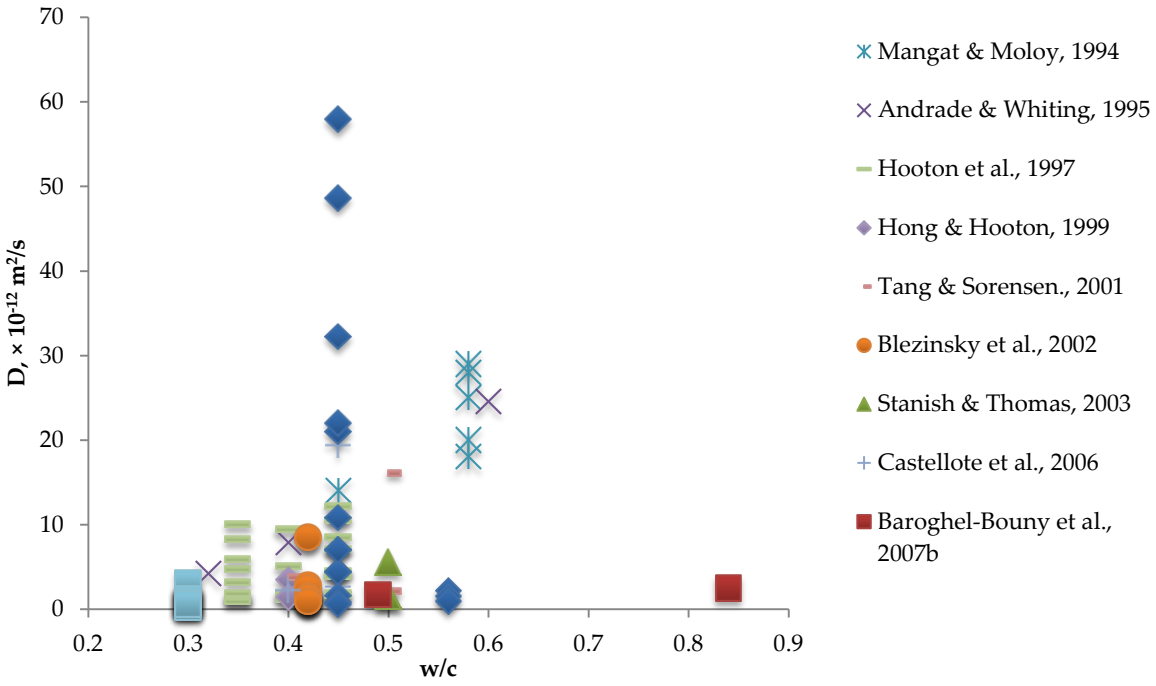


Figure 2.19 Relationship between D_{nss} and water-cement ratio

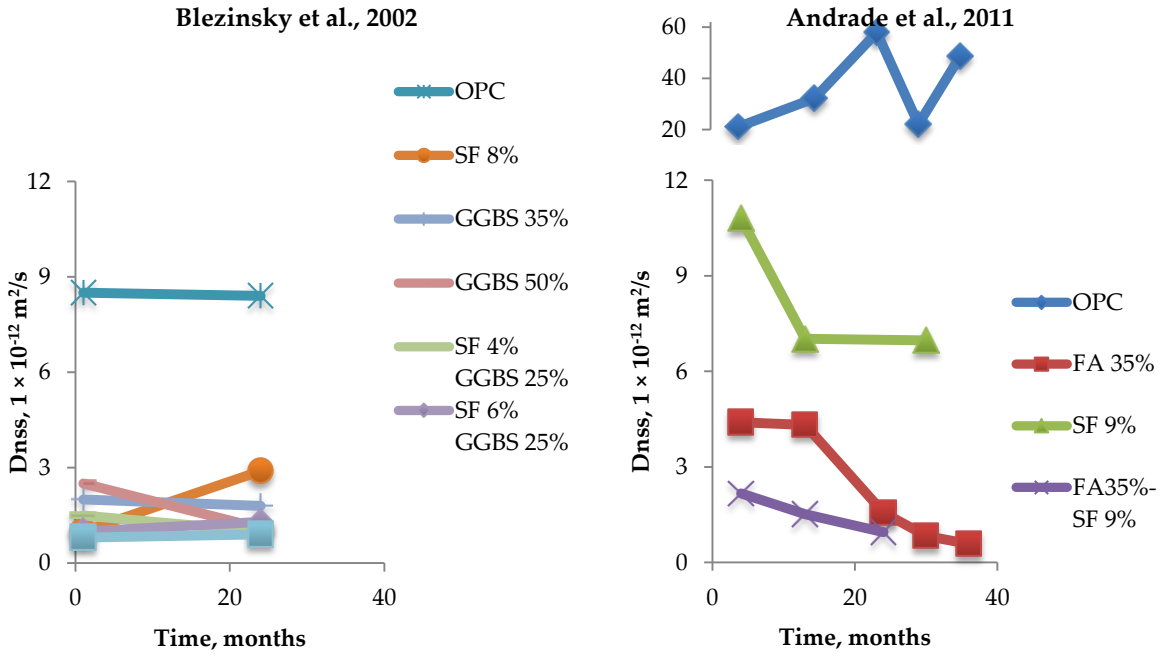


Figure 2.20 Ageing effects with D_{nss} test methods

2.9 EQUIVALENT DURABILITY PERFORMANCE IN EN 206-1 AND BS 8500-1:2006

The term durability performance implies a time dependent durability parameter which is starting to appear in many of the standards and design codes. The way this is being carried out currently is through exposure classes (Bickley et al., 2006a) defined by the deterioration processes. In the EU, this started with EN 206-1. Australia, New Zealand and Canada have also adopted exposure classes in their standards. The countries that use ASTM are also on the move to implement performance-based specification (Bickley et al., 2006a, Bickley et al., 2006b, Bickley et al., 2008).

The equivalent durability performance concept is an extension of the durability performance. It is a tool where performance related test methods are used to compare a new concrete design with a design that has a long standing history of adequate performance locally. Concrete produced through this method will not be subjected to the limiting value specification currently used, thus enabling innovative and more sustainable concrete mix design (Harrison, 2008).

In the current British Standard, item 5.2.5.3 and Annex E and F of BS EN 206-1:2000 and Section A.4 of BS 8500-1:2006 presented a base for the development of this concept as the future way to sustainably specify and design concrete (BSI, 2000b, BSI, 2006a). However, the recommendation of BS EN 206-1:2000 is not fully adopted by the BS 8500-1:2006 with respect to the compressive strength class, maximum water-cement ratio and minimum cement content. Table 2.5 shows the difference between the BS EN 206-1:2000 and BS 8500-1:2006.

It is recognised that over reliance in the standards on maximum water-cement ratio, minimum cement content and compressive strength alone without specifying specific durability requirements directly may result in inadequate protection (Bamforth, 1994). Hooton, et al. (2006) stated that the main hurdle in moving away from a prescriptive-based to a performance based standard is the lack of adequate performance-based durability test methods.

This shows that the value of performance specification of concrete for durability is appreciated and recognised. As understanding of the transport processes grows, so does various standardised test methods to choose from. A practical and acceptable performance-based test method for chloride resistance is achievable.

2.9.1 Philosophy of the approach to the European standard

In spirit, EN 206-1 have embraced performance-based methodology by grouping concrete according to their exposure classes based on its durability performance requirement. In this case the standard covers concrete designed with no risk of corrosion; corrosion induced by carbonation;

corrosion induced by chloride from other than sea water; corrosion induced by chloride from sea water; freeze-thaw attack and lastly chemical attack (BSI, 2000b). However, currently the means of achieving this is still tied to the prescriptive limiting value methodology.

Andrade et al., (2008) stated that at the time of writing the draft for EN 206 during the late 1990s, the performance-based approach had been considered. However, it was regarded as not fully developed for inclusion in EN 206-1. An interim solution has been reached where the performance-based approach havs been entered as an annex in the document. This allowed CEN member countries with confidence in their local test methods to use this approach.

Current durability standards are based on predetermined limiting values that are stipulated in the standard and comprise 'deemed to satisfy' limits on cement content, water-cement, strength class and importantly materials (BSI, 2006a). These limiting values were argued to be impeding new materials and technology from being adopted by the market (Andrade et al., 1999); inhibit efficient use of materials (Hooton et al., 2006) and not directly addressing durability concerns (Alexander et al., 2008). Andrade et al., (2008) also pointed out that the link between the limiting values specified in the current EN 206-1 with established knowledge on the chloride resistance requirement is tenuous.

Neville, (2006b) noted that the move from prescriptive-based specification to the performance-based specification has been comparatively positive. With respect to durability in chloride environment, only just recently in 2011 that CEN has finally agreed a test method to put in place within the European framework.

A plausible cause to this can be seen by looking at the development of performance-based specification within CEN and associated European organisations. It was clear in the report by RILEM TC 116-PCD technical committee of 1999 that, there is a push towards having a fundamental chloride transport coefficient through which both a comparative tool and an input parameter for numerical modelling can be obtained (Andrade et al., 1999). During the same period, the International Federation for Structural Concrete (*fib*) was tasked to develop a model code for service life design – performance-based approach for durability. The model code has since been published in 2006 (fib, 2006) and currently being updated in time of this thesis (fib, 2010).

Andrade et al., (2008) had stated that during the drafting of EN 206-1, RILEM was also asked to review and compare chloride test methods. As a result RILEM TC 178-TMC was created with the

aim of coming up with a test methodology that can be used in modelling of chloride ingress behaviour in concrete.

The members of CEN technical committees, RILEM and *fib* often consist of the same group of people. As a consequence, the approach of the CEN member countries towards chloride test method has always been leaning towards modelling of chloride ingress as it is seen to be able to solve both requirement set out by RILEM TC 116-PCD.

2.9.2 ASTM approach and consequence on the test method

The same cannot be said when discussing the development of American Society for Testing and Materials (ASTM) standard with regards to chloride ingress. ASTM C-1202 test method has clearly been designed as a comparative 'rapid-index' tool (Hooton et al., 2006). In the wording of the standard, the uses include for *'evaluation of materials for design, rapid indication of resistance to chloride penetration and for research purposes'*. It also suggested that the procedure has shown good correlation with American Association of State Highway and Transportation Officials' AASHTO T259 ponding test (ASTM, 1997). However, a large standard error in the test has led to the conclusion that the ASTM C-1202 is useful only to comparatively rank concrete in order of expected resistance (ACI, 1988).

The modelling route for chloride resistance has also been explored by ASTM via ASTM C-1556 test method but it made no reference to a relationship with ASTM C-1202. ASTM C-1556 clearly states that the apparent chloride diffusion coefficient results from the test method are commonly used in chloride ingress modelling.

The point that one tries to convey is that ASTM, and AASTHO for that matter, has elected to separate the comparative tool from the modelling tool. In this regard, comparative performance concept although not explicitly spelled out has been easier to attain in the ASTM user countries compared to Europe.

Table 2.5 Recommendation of BS EN 206-1: 2000 and BS 8500-1:2006 with respect to durability recommendation for the intended working life of 50 years

	BS EN 206-1:2000						BS 8500-1:2006*					
	Chloride from sea water			Chloride from other than sea water			Chloride from sea water			Chloride from other than sea water		
	XS1	XS2	XS3	XD1	XD2	XD3	XS1	XS2	XS3	XD1	XD2	XD3
Maximum w/c	0.50	0.45	0.45	0.55	0.55	0.45	0.40	0.40	0.40	0.45	0.40	0.40
Minimum strength class	C30/37	C35/45	C35/45	C30/37	C30/37	C35/45	C32/40	C32/40	C32/40	C40/50	C32/40	C32/40
Minimum cement content, kg/m^3	300	320	340	300	300	320	380	380	380	360	380	380
Cover depth, mm	-	-	-	-	-	-	30	30	40	25	30	40

* Limiting values as recommended in lowest cover depth.

2.9.3 Reflection on standards development

In reflection, the desire to have a uniform standard with regards to testing potential chloride durability that is applicable throughout the European Economic Community (EEC) may have caused the philosophy and approach of the standard to be different from that of the United States, Canada and other ASTM user countries. With reference to the RILEM TC 116-PCD technical committee which was set up in 1989, the direction of research is pointed more towards having a fundamental chloride transport coefficient for numerical modelling. Furthermore, Neville, (2006a) had commented that part of the problem preparing European standards is because of the different technical and cultural background in the various countries.

Although there are durability requirement in many of the current standards and specifications, they are only based on whatever that is available currently (Hooton et al., 2006). The scientific bases of these tests however, are still being debated and they are likely to continue in this state for quite some time. Problems include mixed results for scatter of data i.e. at times too wide and the basic problem of repeatability and reproducibility. This can be seen in a number of publications on large and medium scale tests (Tang and Sørensen, 2001, Castellote and Andrade, 2001a, Castellote and Andrade, 2001b, Hooton et al., 2006, Castellote et al., 2006).

The revision of EN 206-1 is currently underway and at this stage, there is consensus on the carbonation test and an accelerated test method for chloride diffusion is being put through a round robin test. However, based on the preliminary results it was felt that any of the test method for concrete with respect to chloride may not make it into the current revision of the standard even though CEN TS 12390-11:2010 has been published.

The balance of approach towards equivalent performance and service life modelling is lacking in the European countries compared to the ASTM sector. Pragmatically the novelty of fundamental diffusion coefficient values does appeal to the research community; but the same cannot be said about the practicing engineers who just needed a comparative tool to rank different concrete based on local knowledge in order of resistance to chloride ingress.

2.10 SUMMARY POINTS

The review of literature was undertaken to report the state-of-the-art of the current understanding of the chloride diffusion process and in particular what is established/not established with respect to chloride migration tests. The transport process of chloride into concrete and factors influencing

it have been reviewed. The mathematical treatments of the processes were examined. The author has also dealt with the important topics of chloride binding, pore blocking skin effect and age effects.

The European approach to Equivalent Durability Principles was discussed and test methods to measure the diffusion coefficient were reviewed.

The examination of the literature reveals the following key observations:

i) The transport processes involved in chloride ingress into concrete are multi-faceted and complex involving the effects of the external environment, the local microclimate, and the quality of the concrete. The mathematical treatment of chloride diffusion is made using Fick's Law of Diffusion with accompanying assumptions that are rarely met in real structures. There are attempts by later researchers to propose a more appropriate mathematical treatment but they are too cumbersome for practical use.

ii) The chloride binding phenomenon is an integral part of providing resistance to chloride-induced corrosion. The understanding of this phenomenon is part of the challenge being faced by current researchers and its importance to service life modelling is significant. There are mixed reviews of the pore blocking skin effects. Some studies suggest the effects are significant while others argue the effects are limited.

iii) Concrete's ability to resist chloride ingress improves over time. Ageing factor for concrete resistance to chloride has been suggested by The Concrete Society Report 61 authored by Phil Bamforth. Numerous modelling approaches are being pursued and continually being refined although critical questions such as threshold chloride content and critical chloride content remains elusive. Equivalent Durability Principles may form as a practical intermediate solution to collect data for refinement of the service life models and also as a pragmatic comparative tool for engineers designing new structures.

iv) As yet, there are no benchmark with regards to BS 8500-1:2006 for the performance of the designed concrete intended for 100 years durability based on the prescriptive-based methodology and whether these prescribed concrete at the limit values of the standard could give similar performance with regards to chloride resistance.

v) The review into the migration test methods shows that at cement contents lower than 350 kg/m^3, the effect of lowering the cement content at a water-cement ratio of 0.65 is reduced diffusion coefficient index obtained with the PD test method. At higher cement contents than

350 kg/m^3 and at a water-cement ratio of 0.45, the effect of lowering or increasing the cement content did not seem to be significant. Other factors affecting migration test result reported in the literature are most importantly cement type and water-cement ratio, followed by curing regime, potential difference, cell geometry, aggregate type and conditioning of the specimens.

vi) Analysis on the non steady-state diffusion test data is based on data from similar test methods to the CEN TS12390-11:2010. The same trend emerges with the review of the migration test albeit at a larger magnitude. As the migration tests show a range of results up to 20×10^{-12} m^2/s, the diffusion test based on NT Build 443 shows a range of up to 70×10^{-12} m^2/s.

vii) It is noted that as water-cement ratio decreases, the sensitivity of the available test methods to differentiate the concretes decreases as well. This may mean either the concrete is at the plateau of performance or, the test methods may not be sensitive enough to pick up the difference. The sensitivity of the test method is of concern to the research community as the accuracy of the test methods is of importance in getting a practical estimate for service life modelling.

The current state of the art shows that there is a lack of broad reference data set for the CEN TS 12390-11:2010 test method and this thesis intends to fill the gap. Also, at present there is no benchmark for concrete intrinsic to the limit values of BS 8500-1:2006 for the intended working life of 100 years. This may serve as guidance for future revision of the standard. Effects of several factors on selected chloride resistance test methods as suggested by published literature are summarised in Table 2.6. This will serve as a basis of comparison with results of the experimental works.

Table 2.6 Effect of different factors on chloride test methods

Factors (increase ↑,decrease ↓)	Effects on D	Comments
Cement type	Depends on type	General ranking from better to worse at ≈ 56 day age is SF-ggbs-FA-CEM I
Cement content ↑	↑	Effect often masked due to relationship with w/c.
Water-cement ratio ↓	↓	
Age at test ↑	↓	
Compressive strength ↑	↓	
Exposure solution concentration ↑,↓	Not clear	NT Build 443 = 16.5% NaCl AASHTO T 259 = 3% NaCl An arbitrary volume of ≥ 12.5 ml/cm², 3% NaCl is proposed in the CEN TS 12390-11:2010 justified as adequate for 90 days exposure.
Exposure period	Not clear	A maximum of 90 days is proposed per minimum exposure solution volume.

CHAPTER 3. EXPERIMENTAL PROGRAMME

3.1 INVESTIGATING THE EFFECT OF AGE AT TEST FOR THE CEN TEST METHOD

The current BS 8500-1:2006 standard provides for the concrete specifier and producer with recommendation of mixes for durability especially for the 'designed concrete' approach. Two specific intended working life provisions are stated, 50 years and 100 years respectively. By and large the requirements are the same except higher cover depth required for the 100 year intended working life. Concrete properties and limiting values are arranged according to the nominal cover from 15 mm to 65 mm (BSI, 2006a).

This thesis focuses specifically on the properties and limiting values for 60 mm nominal cover with an intended working life of at least 100 years as described in Table A.5 in the BS 8500-1:2006 standard. This was justified on the reason that typical infrastructure projects especially bridges, whether sea or terrestrial, are often specified similarly. The experimental programme detailing the materials used, concrete mixing procedure, specimen preparation and test methodologies undertaken with respect to the aims and objectives set out in the beginning of the thesis is presented in this chapter.

Figure 3.1 summarises the experimental work programme for the research described in this thesis.

3.1.1 Cements

Portland cement used is 52.5 R cement and conforms to BS EN 197-1:2000 (BSI, 2000a). GGBS used conforms to BS EN 15167-1:2006 (BSI, 2006b). GGBS replacement generally offers the best durability with respect to resistance to chloride ingress compared with Portland cement or fly ash. Additionally, it also improves workability of the mix compared to Portland cement on a similar binder content replacement. As a result in a similar slump class at equal water-cement ratio ratio, ggbs is more workable. This allows for less superplasticising additive requirement.

Fly ash used in this study is category S fineness (≤ 12% retained 45 μm) with category B Loss On Ignition (LOI) (2.0% – 7.0%) fly ash that conforms to BS EN 450-1:2005 (BSI, 2005a). Fly ash is used as cement replacement material at several replacement level of up to 50%. Fly ash also has the added benefit of improved workability and improved durability performance with respect to resistance to chloride ingress compared to Portland cement. After several mixes it was found that the fly ash especially at high cement replacement yields a much lower strength compared to the target strength.

Limestone used in the study conforms to BS 7979:2001 (BSI, 2001). Limestone used in this project is regarded as an inert filler replacement material for Portland cement to lower the overall CO_2 footprint of the concrete. The test programme is reflective of this premise.

Silica fume is supplied in slurry form with a 50:50 (by mass) ratio of water to silica fume and conforms to BS EN 13263:2005 (BSI, 2005b). Silica fume addition in concrete has been regarded as highly durable and able to offer improved durability in chloride laden environment due to their particle packing characteristics. The compressive strength of silica fume concrete is also high at equivalent water-cement ratio ratio compared to Portland cement, ggbs and fly ash concrete.

Properties of binder materials used in all the concrete mixes are presented in Table 3.1.

3.1.2 Aggregates

Coarse aggregates used for the study were sourced locally from a nearby Fife quarry. Two aggregate size gradings were used in the mixes i.e. 4/10 mm and 10/20 mm at a ratio of 35% : 65% respectively after all the other concreting materials calculated with respect to the assumed density of the mix of 2400 kg/m^3. This gravel aggregate had mixed absorption rates influenced by the different materials it consisted of. It is a product of the cycles of glaciations of the last ice ages and has a generally smooth and rounded shape. Due to the features of the aggregate, it is believed they are more influenced by the variation in the laboratory humidity conditions and forms part of the decision to soak the aggregate overnight in the mixing procedure.

Fine aggregates used were sourced from the Fife area similar to the aggregate where it was quarried at the same geographical area. Fine aggregates content was fixed at 42% of total aggregate materials, whilst coarse aggregate made up the remainder. This historically results in good workability while at the same time allows enough coarse aggregates amount to contribute to the compressive strength.

The advantage with this mix design is that it allows the author to focus on the effects of cement materials as the aggregate content (in percentage terms) is fixed. Properties of the aggregates used are presented in Table 3.2. General grading of the aggregates are presented in Table 3.3. Pictures of the aggregates showing each grade size used are presented in Figure 3.2.

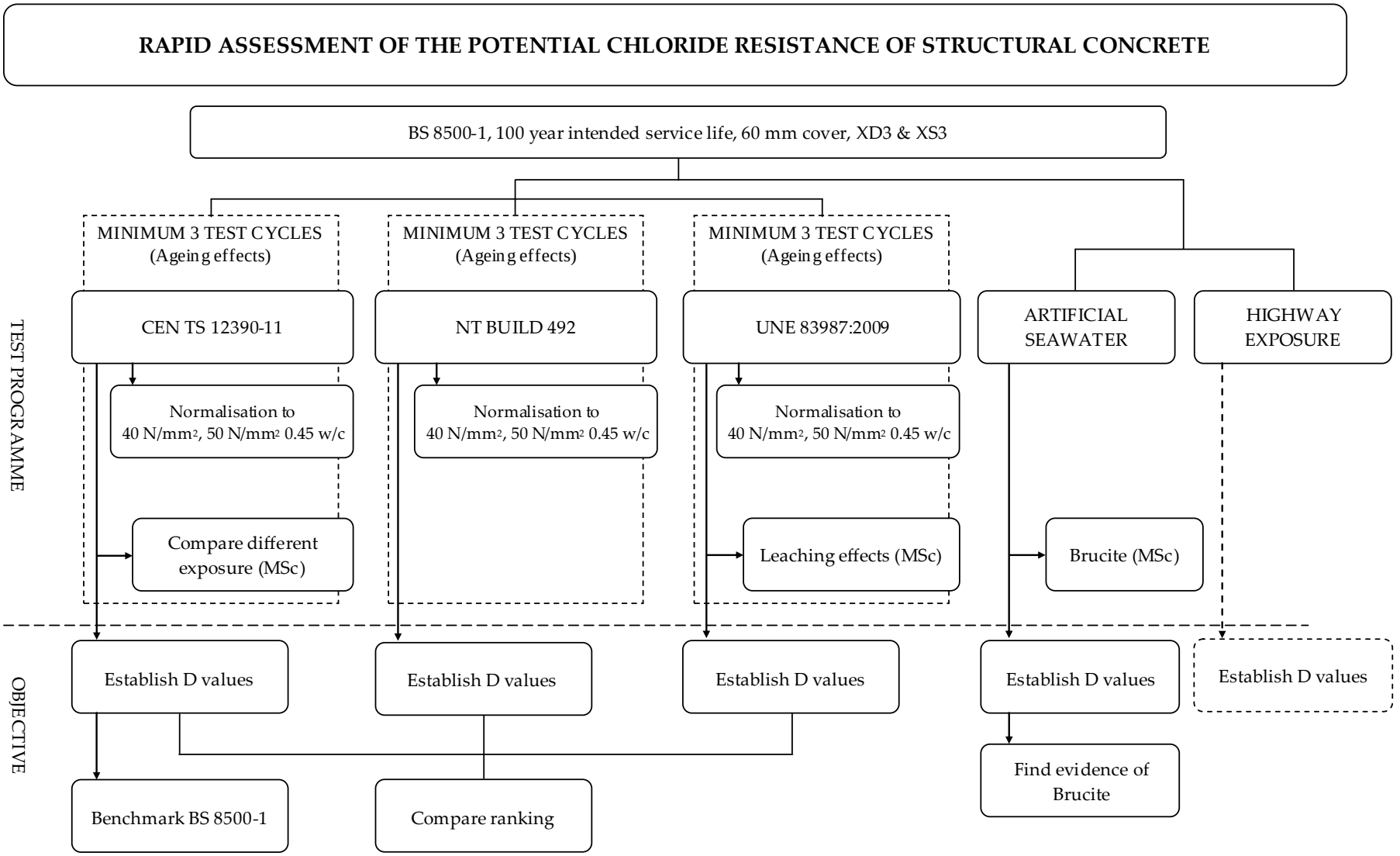


Figure 3.1 Programme of work for the research described in the thesis

Table 3.1 Properties of binder materials used in concrete mixes

	CEM I	Fly ash	Ggbs[A]	Silica fume[A]	Limestone[A]
Specific gravity	3.17	2.26	2.89	2.20	2.63
Blaine fineness, m^2/kg	395	388.5	450	22400	1550
Loss-on-ignition (LOI), %	1.86	6.14	0.90	2.49	42.84
Chloride content	0.03	0.02	-	-	-
Bulk major oxide composition, % by mass					
CaO, %	62.25	3.34	37.97	0.32	55.31
SiO_2, %	19.05	42.13	32.06	97.28	0.43
Al_2O_3, %	4.45	19.65	11.23	0.47	0.28
Fe_2O_3, %	3.01	10.27	0.34	0.07	0.04
MgO, %	0.72	1.30	7.23	0.26	0.14
K_2O, %	0.54	2.70	0.47	0.45	0.00
Na_2O, %	0.28	1.65	0.23	0.16	0.05
SO_3, %	3.24	1.77	0.98	0.12	0.00
Bogue composition, % by mass					
C_3S	6.39	-	-	-	-
C_2S	22.55	-	-	-	-
C_3A	38.33	-	-	-	-
C_4AF	6.73	-	-	-	-

Note:

Bulk major oxide composition determined by XRF

Bogue composition determined by XRD

[A] Values obtained from Dunne, (2010), whose PhD work uses the same supply of materials.

Table 3.2 Properties of aggregates used in concrete mixes

	Natural gravel aggregate		
	Fines	4/10	10/20
Shape, visual	Round	Round	Round
Surface texture, visual	-	Rough	Smooth
Water absorption (laboratory dry to SSD),%	1.0	1.0	1.0
Particle density (SSD), kg/m^3	2600	2600	2600
Bulk density, kg/m^3			
Loose	1580	-	1520
Compacted	1660	-	1610
Loss-on-ignition (LOI), %	3.5	3.5	3.5
Chloride content, %	0.01	0.01	0.01

- Chloride content determined by XRF

Table 3.3 General properties of aggregates

Sieve sizes, mm	Fines	Natural gravel	Sieve sizes, mm	Natural gravel
	0/4	4/10		10/20
	Grading, % passing by mass			
20	-	100	28	100
14	-	99.0	20	90.0
10	-	89.0	16	61.1
6.3	100	25.0	14	40.0
5.0	98.8	11.0	12.7	28.1
4.0	92.5	5.0	10.0	9.0
2.36	85.3	2.1	8.0	4.2
1.18	70.8	-	6.3	1.5
0.60	54.6	-	5.0	1.1
0.30	31.0	-	4.0	0.7
0.15	4.0	-	2.36	0.4
0.075	0.9	-	-	-

The general properties were obtained from Dunne, (2010) who's PhD work uses the same material supply.

Figure 3.2 Aggregates used in the test mixes

3.1.3 Admixtures

A general purpose water reducing admixture and a high range water reducing admixture were used. Both comply with EN 934-2:2009 (BSI, 2009).

3.2 CONCRETE MIXING

Mixing method selection was based on properties of the concrete observed during an earlier mini project and several other observation of concrete mixing procedure done by previous PhD students (Khanna, 2009). Ultimately, soaked aggregates were used and the method is explained below.

This method involves soaking of the coarse aggregate for at least 24 hours. This method avoids the variable workability as a result of the variable absorption rate of the gravel aggregate. Fine aggregates used were laboratory dried by spreading them on the floor for at least 15 hours. Prior to mixing, the coarse aggregates were drained and shaken in perforated buckets for approximately five minutes to discard excess water. The aggregates were saturated and their surface was wet while being weighed. The Water content was adjusted by reducing the quantity added according to the typical aggregate absorption value and the aggregate amount increased. Figure 3.3 illustrates the mixing procedure.

The wet coarse aggregates and the dry fine aggregates were mixed for one minute before the addition of approximately half of the mix water. This is then mixed for another two minutes before being rested under cover for seven minutes to allow for optimum aggregate absorption.

Cement and any powder form binary replacement materials were added before mixing commenced again for one minute. The total water content is mixed in including the admixtures used. Where silica fume is used, it was mixed in with the remaining mix water because the silica fume used in the study was supplied in slurry form. The combined materials were mixed for one minute and then transferred to concrete moulds after slump and plastic density tests.

i. Soaked aggregates are drained prior to mixing

ii. Coarse aggregates in the mixer bowl

iii. Lab dried fine aggregates added

iv. Adding approximately half of mix water after mixing aggregates

v. Cement is added after aggregates have been rested

vi. Remainder of mix water with plasticiser added to finish the mix

vii. Testing for fresh properties

viii. Concrete arranged for 24 hours initial curing under hessian (see Figure 3.4)

Figure 3.3 Concrete mixing procedure

3.3 MIXES FOR THE STUDY

The mixes were designed at the limit state of the durability recommendation for reinforced concrete with an intended working life of at least 100 years. Table A.5 in BS 8500-1:2006. The nominal cover selected is 60 mm and this is used to determine the mix combinations. The ranges of water-cement ratio selected are 0.35 to 0.55. Cement content ranges between 320 kg/m^3 to 380 kg/m^3. From the mix's water-cement ratio and cement content, free water is determined. Fine aggregate content was set at 42% of the cement + water content with a 35% vs. 65% split between the 4/10 mm and the 10/20 mm aggregates for the remainder of the proportion to make up an assumed density of 2400 kg/m^3 across the board. The basic design based on BS 8500-1:2006 is shown in Table 3.4 and Table 3.5. This was done to exclude the effects of aggregate content variation from the experimental procedure as described in Section 3.1.2.

3.4 CONCRETE MIX CONSTITUENT PROPORTIONS

Details of the mixes are presented in Table 3.6. For some of the mixes, the characteristic strength was not achieved. These mixes have high replacement levels and high water-cement ratio. They were re-designed in a second series with lower water-cement ratio to achieve the characteristic strength requirement of BS 8500-1:2006 standard. This is shown in Table 3.7.

3.4.1 Mixing in batches

Between 160-190 kg of concrete havd to be mixed for each mix design. Mixing was done in a rotating pan mixer. The capacity of the concrete mixer is limited to around 90 kg per batch. Due to the high volume of concrete being mixed and the limitation of the concrete mixer, all the mixes had to be done in two batches. Figure 3.4 shows the rotating pan mixer used for all concrete mixing work.

In order to control variation between batches, limiting values for variations have been established. For the fresh concrete, density variation allowed is not less than 20 kg/m^3 with ±10 mm slump difference. Compressive strength at 28 days must not exceed 10% between the batches. Based on this limiting requirement, only three mixes have to be re-cast.

3.4.2 Fresh properties

Fresh properties for the concrete are measured according to BS EN 12350 series. The properties measured are slump and plastic density according to BS EN 12350-2:2000 and BS EN 12350-6:2000 respectively (BSI, 2000c, BSI, 2000d). The results are tabulated in Table 3.8 and Table 3.9.

Table 3.4 Design for 60 mm nominal concrete cover exposure class XD3

Cement/ combinations	Strength class	Maximum w/c	Minimum cement content kg/m³
CEM I, II/A, II/B-S	C40/50	0.40	380
II/B-V, III/A	C28/35	0.50	340
III/B, IV/B-V	C25/30	0.55	320

Table 3.5 Design for 60 mm nominal concrete cover exposure class XS3

Cement/ combinations	Strength class	Maximum w/c	Minimum cement content kg/m³
CEM I, II/A, II/B-S	C45/55	0.35	380
II/B-V, III/A	C28/35	0.50	340
III/B, IV/B-V	C25/30	0.50	340

Figure 3.4 Rotating pan mixer used for all mixing work

Table 3.6 Mix proportion for Series One

Mix code	EN 197 notation	Constituent Proportions (kg/m³)											Admixture
		w/c	Free Water l/m³	Cements						Aggregates			
				PC	GGBS	Fly Ash	Silica Fume	Limestone	Total Cement	Fine	4/10 mm	10/20 mm	
XD Classes mix													
D1	CEM I 52,5 R	0.40	150	380	-	-	-	-	380	785	380	705	1.00
D2	CII/B-V	0.50	170	240	-	100	-	-	340	795	385	710	0.60
D3	CIV/B-V	0.55	175	160	-	160	-	-	320	800	385	720	0.30
D4(R)	CIII/A	0.50	170	170	170	-	-	-	340	795	385	710	0.80
D5	CIII/B	0.55	175	95	225	-	-	-	320	800	385	720	0.45
D6	CII/A-D	0.40	150	350	-	-	30	-	380	785	380	705	0.80
D7	CII/A-LL	0.40	150	320	-	-	-	60	380	785	380	705	0.90
D8	CV/A-M (V-LL)	0.50	170	205	-	100	-	35	340	795	385	710	0.50
D9	CV/A-M (S-D)	0.40	135	155	155	-	30	-	340	810	390	725	1.10
D10	CV/A-M (S-LL)	0.50	170	145	170	-	-	25	340	795	385	710	0.65

Cont'd…

Table 3.6 cont'd…

Mix code	EN 197 notation	Constituent Proportions (kg/m³)											Admixture
		w/c	Free Water l/m³	Cements						Aggregates			
				PC	GGBS	Fly Ash	Silica Fume	Limestone	**Total Cement**	Fine	4/10 mm	10/20 mm	
XS Classes mix													
S1	CEM I 52,5 R	0.35	135	380	-	-	-	-	380	795	380	710	1.80
S2	CII/B-V	0.50	170	240	-	100	-	-	340	795	385	710	0.60
S3	CIV/B-V	0.50	170	170	-	170	-	-	340	795	385	710	0.50
S4	CIII/A	0.50	170	170	170	-	-	-	340	795	385	710	0.80
S5	CIII/B	0.50	170	102	238	-	-	-	340	795	385	710	0.35
S6	CII/A-D	0.35	135	350	-	-	30	-	380	795	380	710	1.40
S7	CII/A-LL	0.35	135	325	-	-	-	55	380	795	380	710	1.50
S8	CV/A-M (V-LL)	0.50	170	205	-	100	-	35	340	795	385	710	0.50
S9	CV/A-M (S-D)	0.40	135	155	155	-	30	-	340	810	390	725	1.10
S10	CV/A-M (S-LL)	0.50	170	145	170	-	-	25	340	795	385	710	0.65

Notes:
Series One - normal characteristics strength; slump S3
- D4(R) is the reference mix; D2=S2; D4=S4; D8=S8; D9=S9; D10=S10
- D8, D9 and D10 are triple blend and not listed in Table 1, BS EN 197-1:2000. Notation follows the nomenclature convention adopted by the standard
- Admixture dosage, per 100 kg of CEM I + combination

Table 3.7 Mix proportion for Series Two

Mix code	EN 197 notation	Constituent Proportions (kg/m³)											
		w/c	Free Water l/m³	Cements						Aggregates			Admixture
				PC	GGBS	Fly Ash	Silica Fume	Limestone	Total Cement	Fine	4/10 mm	10/20 mm	
T1	CIV/B-V	0.40	130	160	-	160	-	-	320	820	395	735	0.50
T2	CIII/B	0.40	130	95	225	-	-	-	320	820	395	735	0.50
T3	CIV/B-V	0.40	135	170	-	170	-	-	340	810	390	725	0.60
T4	CIII/A	0.45	155	170	170	-	-	-	340	800	390	715	0.55

Notes:
Series Two - adjusted to achieve normal characteristic strength; slump S3
- Admixture dosage, per 100 kg of CEM I + combination

3.4.3 Hardened properties

Compressive strength of the hardened concrete was determined according to BS EN 12390-3. Testing was done on 100 mm cubes in triplicates using a digital servo compression tester. The compressive strength data can be viewed in Table 3.10 and Table 3.11.

3.4.4 Production control

To control variation between the two batches of concrete, the mixes that were done together with the cylinder specimens were always used for the lab tests. This involves specimens for the migrations tests and immersion tests. The second batch of the mix was reserved for highway and tidal tank exposure. This way, results from the lab tests are valid as standalone tests without having to validate any intra-batch variation should the need arises. The result from the highway and tidal tank exposure on the other hand can be validated separately if needed.

Fresh concrete were placed in moulds and cured for twenty four hours under damp hessian and polythene sheet. After twenty four hours they were de-moulded and placed in water curing tanks temperature controlled between 18 °C to 23 °C for at least twenty eight days before the first of the tests commenced. The early curing procedure is pictured in Figure 3.5.

After twenty eight days, the first of the specimens for CEN test and rapid test are cut and put it their respective tests. Specimen for cyclic wetting exposure and site exposure were placed at their respective sites. All other specimens were kept under water until the time of testing.

Table 3.8 Fresh properties for Series One

Mix code	EN 197 notation	Constituent Proportions (kg/m³)								*Achieved Density, kg/m³*	*Achieved Consistency (slump), mm*
				Cements			Aggregates				
		w/c	**Free Water** l/m³	PC	Total Addition	**Total Cement**	Fine	4/10 mm	10/20 mm		
Reference mix											
R(D2)	CII/B-V	0.50	170	240	100	340	795	385	710	*2400*	*195*
XD Classes mix											
D1	CEM I 52,5 R	0.40	150	380	-	380	785	380	705	*2380*	*105*
D2	CII/B-V	0.50	170	240	100	340	795	385	710	*2400*	*195*
D3	CIV/B-V	0.55	175	160	160	320	800	385	720	*2330*	*170*
D4	CIII/A	0.50	170	170	170	340	795	385	710	*2305*	*175*
D5	CIII/B	0.55	175	95	225	320	800	385	720	*2350*	*125*
D6	CII/A-D	0.40	150	350	30	380	785	380	705	*2425*	*193*
D7	CII/A-LL	0.40	150	320	60	380	785	380	705	*2470*	*195*
D8	CV/A-M (V-LL)	0.50	170	205	135	340	795	385	710	*2410*	*190*
D9	CV/A-M (S-D)	0.40	135	155	185	340	810	390	725	*2435*	*70*
D10	CV/A-M (S-LL)	0.50	170	145	195	340	795	385	710	*2315*	*180*

* The reference mix R is the same with D2

All proportions rounded to the nearest 5 kg/m³

Cont'd…

Table 3.8 Cont'd…

Mix code	EN 197 notation	Constituent Proportions (kg/m³)								*Achieved Density, kg/m³*	*Achieved Consistency (slump), mm*
				Cements			Aggregates				
		w/c	Free Water l/m³	PC	Total Addition	**Total Cement**	Fine	4/10 mm	10/20 mm		
XS Classes mix											
S1	CEM I 52,5 R	0.35	135	380	-	380	795	380	710	*2435*	*65*
S2	CII/B-V	0.50	170	240	100	340	795	385	710	*2400*	*195*
S3	CIV/B-V	0.50	170	170	170	340	795	385	710	*2430*	*215*
S4	CIII/A	0.50	170	170	170	340	795	385	710	*2305*	*175*
S5	CIII/B	0.50	170	102	238	340	795	385	710	*2430*	*185*
S6	CII/A-D	0.35	135	350	30	380	795	380	710	*2450*	*130*
S7	CII/A-LL	0.35	135	325	55	380	795	380	710	*2470*	*210*
S8	CV/A-M (V-LL)	0.50	170	205	135	340	795	385	710	*2410*	*190*
S9	CV/A-M (S-D)	0.40	135	155	185	340	810	390	725	*2435*	*70*
S10	CV/A-M (S-LL)	0.50	170	145	195	340	795	385	710	*2315*	*180*

N.B. D2=S2; D4=S4;D8=S8;D9=S9;D10=S10

All proportions rounded to the nearest 5 kg/m³

Table 3.9 Fresh properties for Series Two

Mix code	EN 197 notation	Constituent Proportions (kg/m³)								*Achieved Density, kg/m³*	*Achieved Consistency (slump), mm*
				Cements			Aggregates				
		w/c	**Free Water** l/m³	PC	Total Addition	**Total Cement**	Fine	4/10 mm	10/20 mm		
T1	CIV/B-V	0.40	130	160	160	320	820	395	735	*2410*	*110*
T2	CIII/B	0.40	130	95	225	320	820	395	735	*2425*	*160*
T3	CIV/B-V	0.40	135	170	170	340	810	390	725	*2465*	*60*
T4	CIII/A	0.45	155	170	170	340	800	390	715	*2385*	*200*

All proportions rounded to the nearest 5 kg/m³

Table 3.10 Hardened properties for Series One

Mix code	EN 197 notation	Constituent Proportions (kg/m³)								*Target strength, N/mm² @ 28 days*	*Achieved strength, N/mm² @ 28 days*	*Achieved strength, N/mm² @ 1 year*
		w/c	Free Water l/m³	Cements			Aggregates					
				PC	Total Addition	**Total Cement**	Fine	4/10 mm	10/20 mm			
Reference mix												
R(D2)	CII/B-V	0.50	170	240	100	340	795	385	710	*35*	*31.0*	*51.0*
XD Classes mix												
D1	CEM I 52,5 R	0.40	150	380	-	380	785	380	705	*50*	*53.5*	*60.5*
D2	CII/B-V	0.50	170	240	100	340	795	385	710	*35*	*31.0*	*51.0*
D3	CIV/B-V	0.55	175	160	160	320	800	385	720	*30*	*12.0*	*39.0*
D4	CIII/A	0.50	170	170	170	340	795	385	710	*35*	*25.0*	*43.5*
D5	CIII/B	0.55	175	95	225	320	800	385	720	*30*	*23.0*	*51.0*
D6	CII/A-D	0.40	150	350	30	380	785	380	705	*50*	*62.0*	*73.0*
D7	CII/A-LL	0.40	150	320	60	380	785	380	705	*50*	*60.0*	*74.0*
D8	CV/A-M (V-LL)	0.50	170	205	135	340	795	385	710	*35*	*31.5*	*51.5*
D9	CV/A-M (S-D)	0.40	135	155	185	340	810	390	725	*35*	*51.5*	*74.5*
D10	CV/A-M (S-LL)	0.50	170	145	195	340	795	385	710	*35*	*30.0*	*40.0*

All proportions rounded to the nearest 5 kg/m³

Cont'd…

Table 3.10 Cont'd…

Mix code	EN 197 notation	Constituent Proportions (kg/m³)								*Target strength, N/mm² @ 28 days*	*Achieved strength, N/mm² @ 28 days*	*Achieved strength, N/mm² @ 1 year*
		w/c	Free Water l/m³	Cements			Aggregates					
				PC	Total Addition	**Total Cement**	Fine	4/10 mm	10/20 mm			
XS Classes mix												
S1	CEM I 52,5 R	0.35	135	380	-	380	795	380	710	*55*	*62.5*	*70.5*
S2	CII/B-V	0.50	170	240	100	340	795	385	710	*35*	*31.0*	*51.0*
S3	CIV/B-V	0.50	170	170	170	340	795	385	710	*30*	*16.0*	*43.0*
S4	CIII/A	0.50	170	170	170	340	795	385	710	*35*	*25.0*	*43.5*
S5	CIII/B	0.50	170	102	238	340	795	385	710	*30*	*27.5*	*49.5*
S6	CII/A-D	0.35	135	350	30	380	795	380	710	*55*	*78.0*	*82.0*
S7	CII/A-LL	0.35	135	325	55	380	795	380	710	*55*	*57.0*	*70.5*
S8	CV/A-M (V-LL)	0.50	170	205	135	340	795	385	710	*35*	*31.5*	*51.5*
S9	CV/A-M (S-D)	0.40	135	155	185	340	810	390	725	*35*	*51.5*	*74.5*
S10	CV/A-M (S-LL)	0.50	170	145	195	340	795	385	710	*35*	*30.0*	*40.0*

N.B. D2=S2; D4=S4;D8=S8;D9=S9;D10=S10

All proportions rounded to the nearest 5 kg/m³

Table 3.11 Hardened properties for Series Two

Mix code	EN 197 notation	Constituent Proportions (kg/m³)								*Target strength, N/mm² @ 28 days*	*Achieved strength, N/mm² @ 28 days*	*Achieved strength, N/mm² @ 1 year*
				Cements			Aggregates					
		w/c	**Free Water** l/m³	PC	Total Addition	**Total Cement**	Fine	4/10 mm	10/20 mm			
T1	CIV/B-V	0.4	130	160	160	320	820	395	735	*30*	*29.5*	*56.5*
T2	CIII/B	0.4	130	95	225	320	820	395	735	*35*	*38.0*	*59.0*
T3	CIV/B-V	0.4	135	170	170	340	810	390	725	*30*	*42.5*	*54.5*
T4	CIII/A	0.45	155	170	170	340	800	390	715	*30*	*29.0*	*61.0*

All proportions rounded to the nearest 5 kg/m³

Figure 3.5 Curing procedure during the first 24 hours

3.5 NORMALISATION OF RAW DATA FOR INTERCOMPARISON PURPOSES

Due to the heavy concrete mixing load and limited time and resources for testing, it was decided to spread out the testing program and normalise collected data instead of testing all mixes at a specific point of time. This has the advantage of being able to aggregate groups of mixes done at a relatively similar time period into a manageable work package. Time was then freed to focus on one test at a time and thus to avoid mistakes and confusion. The disadvantage of this method is that not all data are obtained at the same age.

To overcome the problem of data not coming from the same age of test, interpolation of the diffusion coefficient and other relevant data plotted against test age is considered a practical solution.

3.5.1 Procedure for the normalisation of the raw data

The results of the experimental programme was normalised to allow interpolation of data for equal test age between different tests. Figure 3.6 shows the example of the normalisation procedure with respect to interpolating expected diffusion coefficient values at 50 weeks age between all three test methods. Table 3.12 to Table 3.14 shows the normalised mix constituent for each of the normalisation criteria namely 40 N/mm^2, 50 N/mm^2 target strength at 28 days and 0.45 water-cement ratio. Normalised data plot can be referred to in APPENDIX D.

Mix normalisation for equal compressive strength was carried out by interpolating achieved compressive strengths to the water-cement ratio of the mixes for each mix. Once the water-cement ratio for each normalised strength was established, the cement content was determined based on the relationship between cement content and water-cement ratio. With the water-cement ratio and cement content established, other elements of the mix namely the amount of free water, and aggregate content could be determined based on their relationship with the same water-cement ratio.

The normalisation of the mixes to 0.45 water-cement ratio follows the same principle as above except the mix proportions were based on the compressive strength of the normalised mixes, interpolated at 0.45 water-cement ratio.

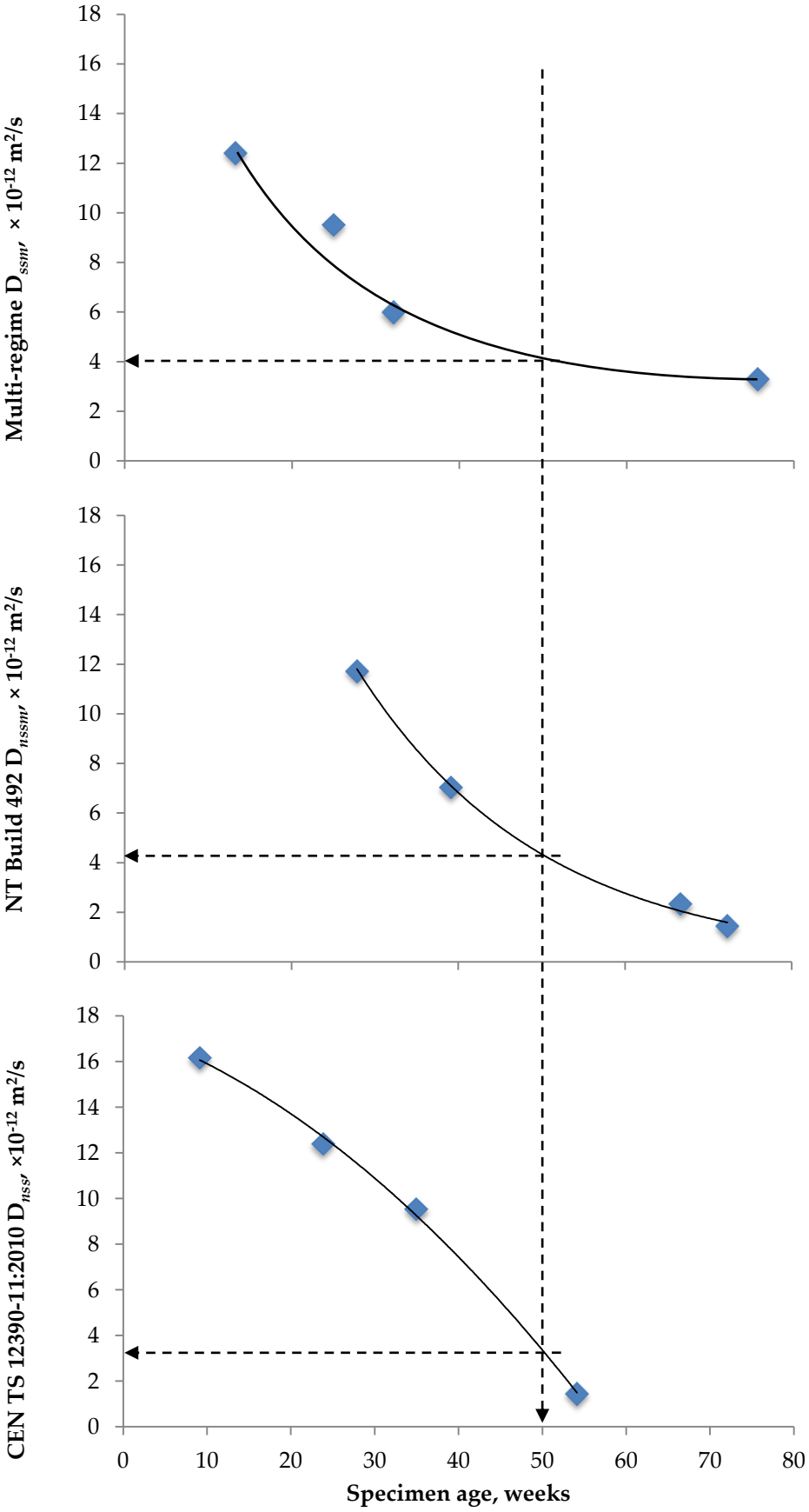


Figure 3.6 **Example of normalisation procedure to interpolate test age and expected test results for all three test methods**

Table 3.12 Normalised mix constituent proportions to 40 N/mm²

Mix code	EN 197 notation	Proportions	Constituent Proportions (kg/m³)							
			w/c	Free Water l/m³	Cements			Aggregates		
					PC	Total Addition	**Total Cement**	Fine	4/10 mm	10/20 mm
N1	CEM I 52,5 R	100% PC	0.51	170	335	–	335	795	385	715
N2	CII/B-V	70% PC + 30% FA	0.42	150	250	110	360	770	390	730
N3	CIV/B-V	50% PC + 50% FA	0.35	130	185	185	370	800	385	715
N4	CIII/A	50% PC + 50% GGBS	0.44	150	170	170	340	800	390	720
N5	CIII/B	30% PC + 70% GGBS	0.41	135	100	225	325	815	395	730
N6	CII/A-D	92% PC + 8% SF	0.56	210	345	30	375	760	370	685
N7	CII/A-LL	85% PC + 15% Limestone	0.54	170	265	50	315	805	390	720
N8	CV/A-M (V-LL)	60% PC + 10% Limestone + 30% FA	0.42	150	215	145	360	795	385	710
N9	CV/A-M (S-D)	46% PC + 46% GGBS + 8% SF	0.44	150	155	185	340	800	390	720
N10	CV/A-M (S-LL)	43% PC+ 7% Limestone + 50% GGBS	0.45	155	150	195	345	800	385	715

Table 3.13 Normalised mix constituent proportions to 50 N/mm²

Mix code	EN 197 notation	Proportions	Constituent Proportions (kg/m³)							
			w/c	Free Water l/m³	Cements			Aggregates		
					PC	Total Addition	**Total Cement**	Fine	4/10 mm	10/20 mm
N1	CEM I 52,5 R	100% PC	0.43	155	360	–	360	785	385	715
N2	CII/B-V	70% PC + 30% FA	0.36	135	265	115	380	770	390	725
N3	CIV/B-V	50% PC + 50% FA	0.33	130	200	200	400	785	380	705
N4	CIII/A	50% PC + 50% GGBS	0.40	150	185	185	370	810	375	695
N5	CIII/B	30% PC + 70% GGBS	0.37	140	265	110	375	825	370	690
N6	CII/A-D	92% PC + 8% SF	0.48	170	325	30	355	790	380	705
N7	CII/A-LL	85% PC + 15% Limestone	0.46	160	300	50	350	790	385	715
N8	CV/A-M (V-LL)	60% PC + 10% Limestone + 30% FA	0.36	135	230	150	380	790	385	710
N9	CV/A-M (S-D)	46% PC + 46% GGBS + 8% SF	0.40	150	170	200	370	790	380	710
N10	CV/A-M (S-LL)	43% PC+ 7% Limestone + 50% GGBS	0.41	150	155	210	365	790	385	710

Table 3.14 Normalised mix constituent proportions to 0.45 water-cement ratio

Mix code	EN 197 notation	Proportions	Constituent Proportions (kg/m³)							
			compres. Strength N/mm²	Free Water l/m³	Cements			Aggregates		
					PC	Total Addition	**Total Cement**	Fine	4/10 mm	10/20 mm
N1	CEM I 52,5 R	100% PC	47	165	365	–	365	790	378	702
N2	CII/B-V	70% PC + 30% FA	36	160	250	105	355	770	390	725
N3	CIV/B-V	50% PC + 50% FA	23	155	170	170	340	805	385	715
N4	CIII/A	50% PC + 50% GGBS	37	155	170	170	340	800	387	718
N5	CIII/B	30% PC + 70% GGBS	33	150	100	230	330	805	390	725
N6	CII/A-D	92% PC + 8% SF	53	165	335	30	365	775	383	712
N7	CII/A-LL	85% PC + 15% Limestone	50	165	310	55	365	790	378	702
N8	CV/A-M (V-LL)	60% PC + 10% Limestone + 30% FA	36	160	215	140	355	770	390	725
N9	CV/A-M (S-D)	46% PC + 46% GGBS + 8% SF	40	155	155	185	340	800	387	718
N10	CV/A-M (S-LL)	43% PC+ 7% Limestone + 50% GGBS	38	155	145	195	340	800	387	718

3.6 EXPERIMENTAL DETAILS

3.6.1 Diffusion test

The CEN TS-12390-11:2010 was recently confirmed as a Technical Specification by CEN (CEN, 2010). This is the last step before upgrading to the full European Standard status. Unlike the conventional natural diffusion test that deals with steady-state diffusion, i.e. chloride binding is ignored, the test measures the non steady-state diffusion. Steady-state natural diffusion test takes upwards to a year to complete while this non steady-state version takes only 90 days.

The specimens for this test were cut using a water cooled diamond saw. It is important that the specimen is cut in a parallel line to the cast surface during this procedure. This is to make sure that during profile grinding, the depth of the layers are uniform at different measurement points of the profile. Figure 3.7 shows the schematic representation of cutting procedure while Figure 3.8 shows the test procedure including profile grinding.

After cutting, the specimens were vacuum saturated. This involves placing the samples in a desiccator and pumping air out using vacuum pump capable of maintaining absolute pressure of 5 kPa for 3 hours and later introducing distilled or deionised water while vacuum is running for a further 1 hour making sure the specimens are submerged. After 4 hours of vacuum saturation the vacuum pump was turned off and the specimens were left to sit in the deionised water for a minimum of 18 hours to ensure complete saturation.

Paraffin wax was then applied to the specimens to seal all the sides except the cut face to be exposed in the chloride solution. The specimens were then immersed in saturated $Ca(OH)_2$ solution for a minimum of 18 hours before being wrapped in cling film. This step is a double protection to ensure that if the paraffin wax breaks during the exposure period, the seal will still be intact.

Immersion test was done using an airtight container with the capacity of 4.12 l. The minimum requirement for the chloride solution is 1.25 l per 100 cm^2 surface. This airtight container is therefore capable to house two cut cube specimens with the dimension of 70 mm × 100 mm × 100 mm. The maximum depth for chloride penetration thus equals to 70 mm although the penetration would rarely be more than 30 mm deep depending on the quality of the concrete given the test duration is only 90 days.

Every airtight container contains 2.62 L of 3% chloride solution for 200 cm^2 exposed surface. Using the same type of container for each immersion test reduces the possible variability of different

volume of solution. Finally the specimens were covered and kept in an environmental chamber, temperature controlled to 22 °C ±2 °C for 90 days or more.

A set of three mixes each was also tested for the evolution of their non-steady state diffusion coefficient value at 30, 60, 90 and 120 days. These are Mix D2 which is the reference mix, D4 and D7. These mixes represent binary mixes each for fly ash, ggbs and CEM I + limestone respectively. The objective of this exercise was to determine the consistency of the rate of diffusion across different cements. For that matter, NaCl solution was not changed after 90 days as recommended by the test procedure in CEN TS 12390-11:2010 (CEN, 2010).

3.6.1.1 Profile grinding

The specimens were taken out from the airtight container after 90 days exposure. They were left to dry for a minimum of 2 hours in lab air before profile grinding. It was recommended in the technical specification that specimens taken out from the exposure must be ground within 8 hours. The recommendation was followed. The standard specifies a minimum of 8 layers. Table 3.15 shows the recommended depth intervals for CEM I and Table 3.16 show the layer depth recommended for binary and ternary replacement with ggbs, fly ash or silica fume.

Concrete powder was grounded using the Germann Instruments profile grinder kit. It consists of a speed-variable handheld grinder unit with a diamond tip bit. Backing plate holding the clamp fixture is mounted on the wall. 75 mm thick specimens are housed in a grinding plate attached to the wall mounted backing plate. The profile grinder is able to profile layers accurately between 0.5 mm to 1.0 mm.

It has to be noted that the grinding process is time consuming. A single sample takes about 40 minutes to profile into eight layers. As a typical set comprises 3 specimens, 2 hours is needed for a single mix. The accuracy of the depth has to be controlled and profiled depths are measured at three points every layer within the specimens.

To obtain a representative sample, the profile area has to be more than three times the nominal area of the aggregate. In this case, the minimum profile area has to be controlled to no less than 60 mm^2.

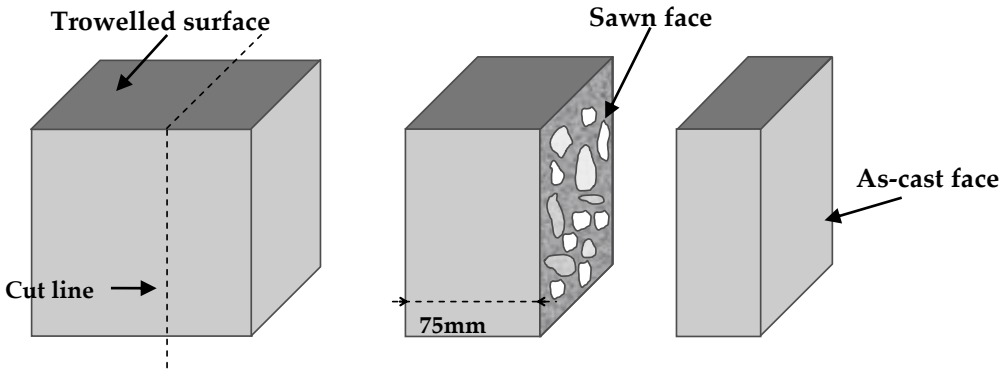


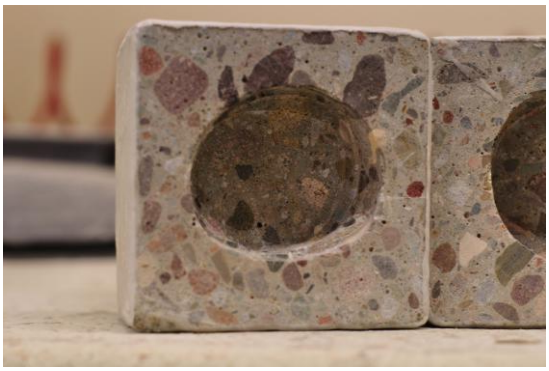
Figure 3.7 100 × 100 × 100 mm cube specimens used for immersion test

i. Specimens cut using water cooled diamond saw

ii. Vacuum saturation before applying paraffin wax

iii. Storage of specimens for 90 days in airtight container in the environmental chamber

iv. After the 90 days exposure period, specimens are ground with a profile grinder machine



v. View of specimen after grinding of 8 layers

vi. Collected samples in self sealing plastic bags

Figure 3.8 Immersion test procedure

Table 3.15 Recommended depth intervals (millimetres) of profile grinding for CEM I concrete (CEN, 2010)

w/c	0.30	0.35	0.40	0.50	0.60	0.70
Layer 1	0~1	0~1	0~1	0~1	0~1	0~1
Layer 2	1~2	1~2	1~3	1~3	1~3	1~5
Layer 3	2~3	2~3	3~5	3~5	3~6	5~10
Layer 4	3~4	3~5	5~7	5~8	6~10	10~15
Layer 5	4~6	5~7	7~10	8~12	10~15	15~20
Layer 6	6~8	7~9	10~13	12~16	15~20	20~25
Layer 7	8~10	9~12	13~16	16~20	20~25	25~30
Layer 8	10~12	12~16	16~20	20~25	25~30	30~35

Table 3.16 Recommended depth intervals (millimetres) of profile grinding for concrete containing ggbs, fly ash or silica fume (CEN, 2010)

w/c [a)]	0.30	0.35	0.40	0.50	0.60	0.70
Layer 1	0~1	0~1	0~1	0~1	0~1	0~1
Layer 2	1~2	1~2	1~2	1~3	1~3	1~3
Layer 3	2~3	2~3	2~3	3~5	3~5	3~6
Layer 4	3~4	3~4	3~5	5~7	5~8	6~10
Layer 5	4~5	4~6	5~7	7~10	8~12	10~15
Layer 6	5~6	6~8	7~9	10~13	12~16	15~20
Layer 7	6~8	8~10	9~12	13~16	16~20	20~25
Layer 8	8~10	10~12	12~16	16~20	20~25	25~30

[a)]Where the concrete contains a Type II addition, the w/c ratio is replaced with a $w/(c + k \cdot a)$ ratio. k values can be referred to in EN 206-1.

3.6.1.2 Acid soluble chloride by titration

The chloride content was determined through the acid soluble chloride method as determined by CEN TS 12390-11:2010. The method is described in BS EN 14629:2007 (BSI, 2007). This test originates from BS EN 1744-5:2006 (BSI, 2006c) t for dredged aggregates to determine their chloride content. The percentage of chloride detected through this method is about 80% - 94% of the total chloride content measured by XRF, as reported by Dhir et al., (1990a). Potentiometric titration was used as this method has the advantage of being automated thus quicker than manual titration using the Volhard method.

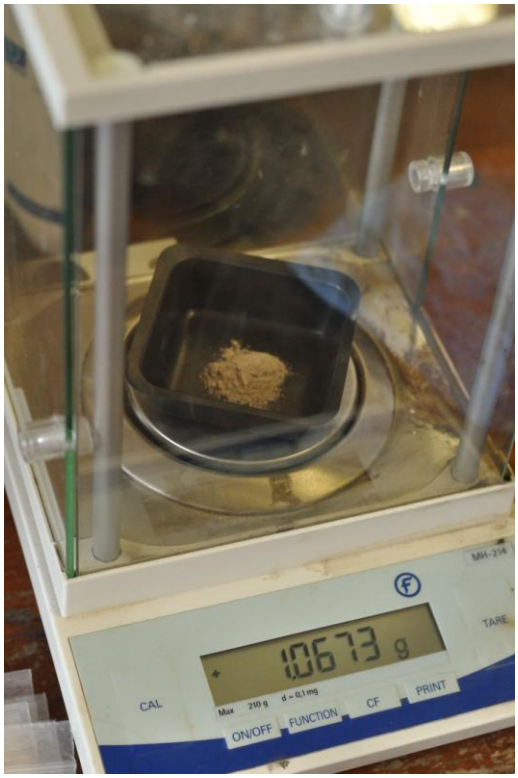
The acid soluble chloride content was established by boiling approximately one gram of profiled sample in 100 mm distilled deionised water acidified with 10 ml, 5 M nitric acid (HNO_3). Boiling takes place on a hotplate magnetic stirrer with the temperature set at 175 °C. The solution was boiled with continuous stirring between 3 - 5 minutes. A secondary hotplate was used to bring the temperature of the solution up to the boil. This setup allows a continuous exchange of beakers every 4 - 5 minutes. Figure 3.9 shows the acid digestion and titration process.

After boiling, the solution was allowed to cool to room temperature before conducting chloride titration using Metrohm 716 DMS Titrino autotitrator. This unit is controlled by TiNet 2.4 software on the computer. To improve efficiency, Metrohm 730 sample changer was used and samples are titrated in series of eight layer samples (one complete specimen) at a time. Figure 3.10 shows a typical result of a single titration cycle.

The automatic titration measures the amount of silver nitrate used via potentiometric titration. This is where the chloride ions are reacted with the silver nitrate ($AgNO_3$) in small increments and the change in potential of the solution is monitored. The endpoint is reached when all chloride ions have reacted with the $AgNO_3$ and precipitated as silver chloride (AgCl). The volume of $AgNO_3$ at the endpoint is recorded and chloride ion content by mass of concrete (CC) is calculated as:

$$\boldsymbol{CC = 3.545f(V_4 - V_3)/m} \qquad \textbf{Equation 3.1}$$

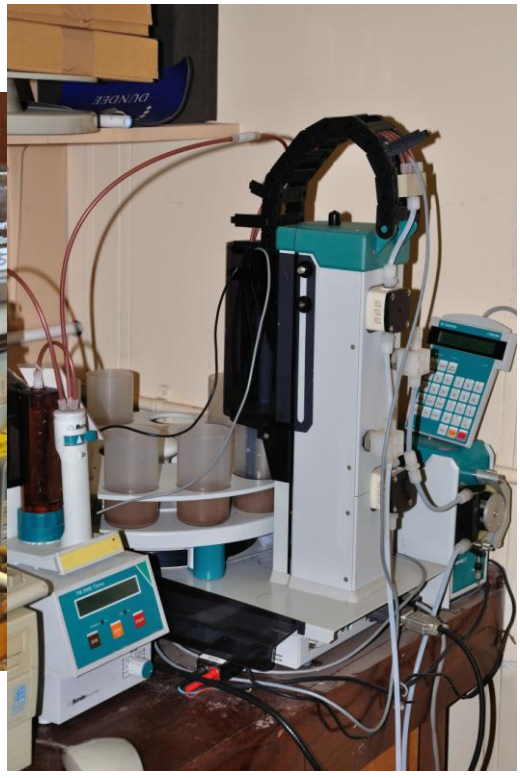
Where: V_3 = volume of the $AgNO_3$ solution used in the titration, ml; V_4 = volume of the $AgNO_3$ solution used in the blank titration, ml; m = mass of the concrete sample, g; f = molarity of the $AgNO_3$ solution.



i. Samples are weighed to accurate to 2 decimal places and placed in beaker containing 50 ml deionised water.

ii. 10 ml, 5 M nitric acid is added before adding 50 ml hot water

iii. Boiling of the acidified solution on a magnetic stirrer hotplate for 3-4 minutes



iv. After the solution has cooled down to room temperature, titration is conducted

Figure 3.9 Procedure for acid soluble chloride determination following BS EN 14629

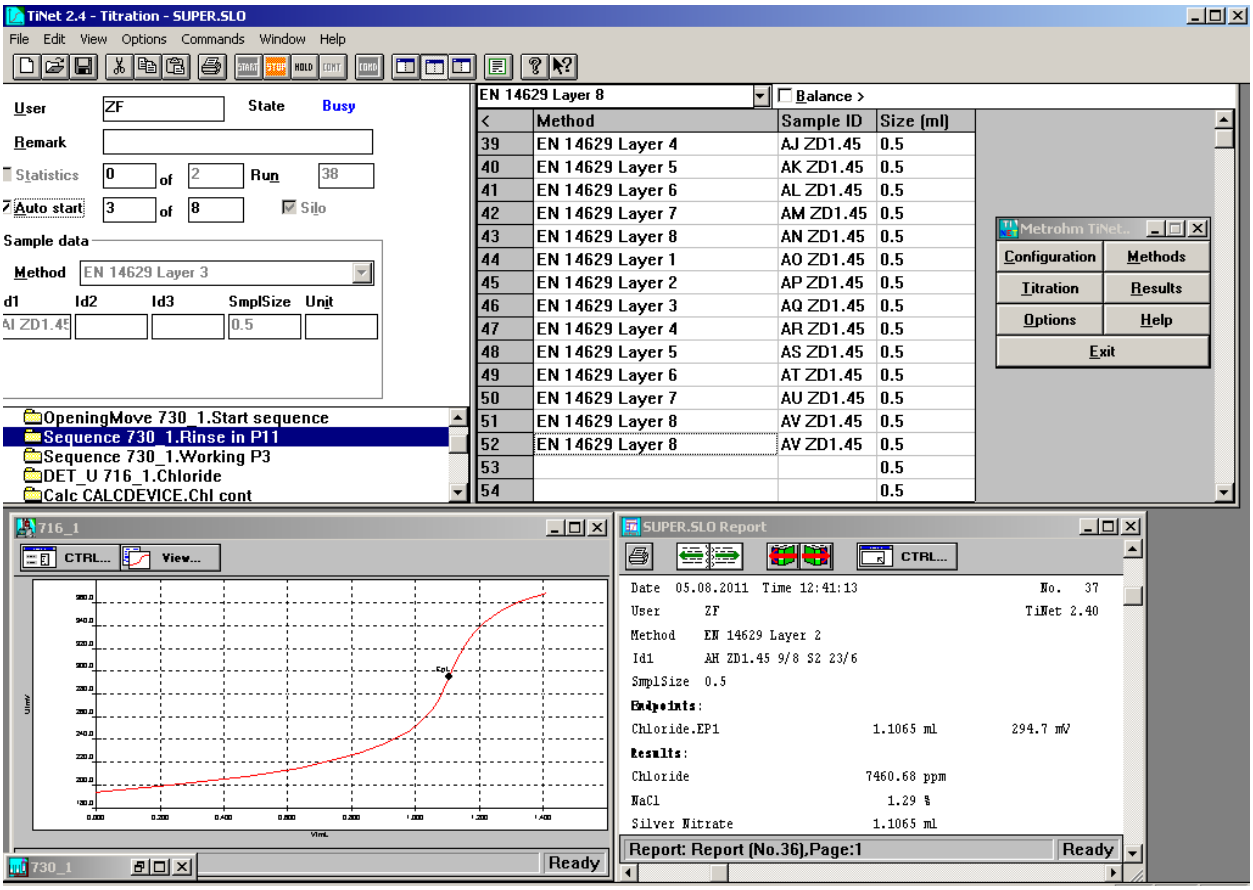


Figure 3.10 Typical screen view for titration using TiNet2.4

3.6.1.3 Cs determination

One of the problems with the test method was the determination of surface chloride content (C_s). There is no consensus within the research community currently as to how to measure C_s. For the purpose of this work, C_s was determined using the Excel's Visual Basic for Application (VBA) script function programmed by Tang Luping from Chalmers University of Technology, Sweden shown in Figure 3.11. The script was programmed based on the premise that the non-linear regression of the least squares fit method is a partial derivative of the equation:

$$\boldsymbol{C(x,t) = C_s - (C_s - C_i) \cdot erf\left(\frac{x}{\sqrt{4D_{nss}t}}\right)} \qquad \textbf{Equation 3.2}$$

This equation was used to determine both C_s and the diffusion coefficient, D_{nss}. The first data point was discarded and regression analysis uses the second data point onwards until the chloride content value is between initial chloride content (C_i) and C_i + 0.015%. Data that lies lower than this value are excluded. C_s value is calculated automatically by the VBA script using the average transport coefficient value generated from data used in the regression analysis.

Other methods were also tried to determine C_s. Firstly, a simple method of using the linear function to the second, third and fourth data point and moving backward to the y-axis intercept. It was found that this causes an underestimation of C_s especially on the higher binding capacity mixes characterises by a non-linear plot.

Secondly the polynomial trendline function (2 or 3 order depending on the visual shape of the curve) in excel was tried unsatisfactorily. The points taken for the determination is based on the general rule of discarding the first data point and in this case, moving forward until the difference of values between two points is not less than 0.05. Additionally, the difference must be above the C_i value. Intercept value at y-axis is then calculated using the excel function and taken as the C_s value. At this point, unless there is a broad agreement on how to determine C_s value, it is as much as a guesswork.

3.6.1.4 Calculation of diffusion coefficient

Once the C_s was obtained the calculation of the non-steady state diffusion coefficient is determined by fitting Equation 3.2 to the data points by means of non-linear regression analysis of least squares shown in Figure 3.12.

Tang's VBA script application also calculates the diffusion coefficient from the supplied data following the Equation 3.2 which is identical to the solution to the CEN TS 12390-11:2010. The solution has been programmed into the script and calculated automatically together with C_s.

Where data point does not follow normal distribution within three measurements it was treated as an outlier and excluded from the calculations.

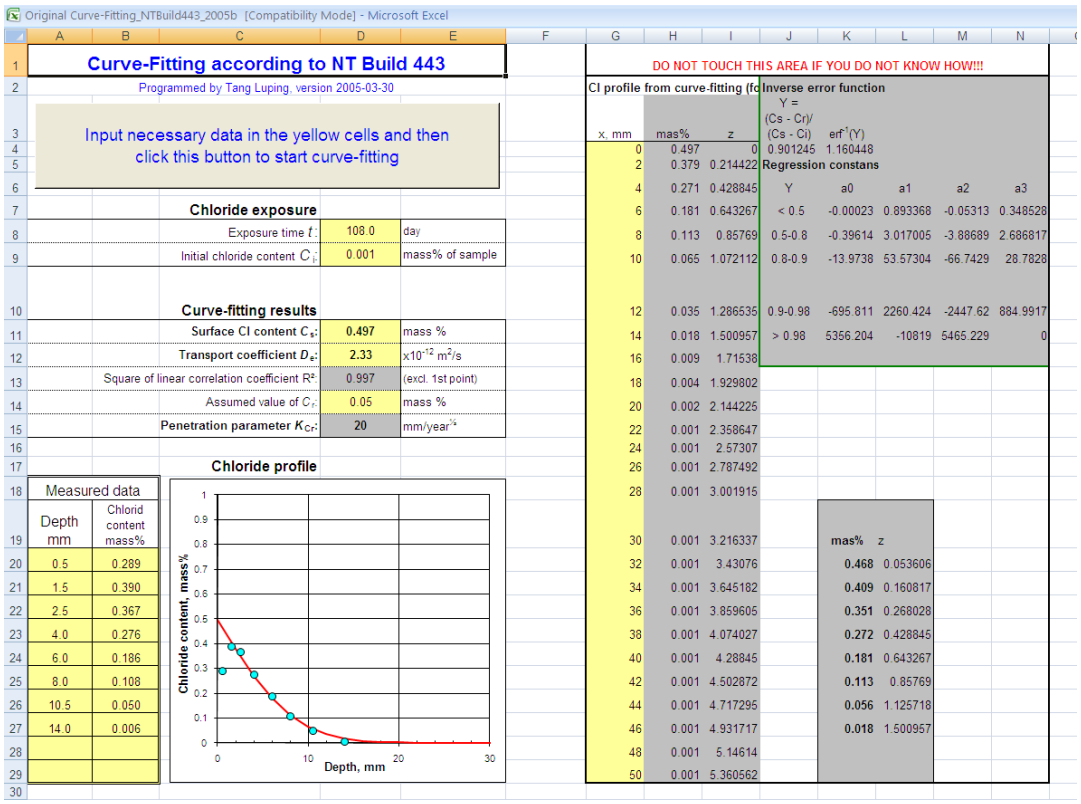


Figure 3.11 Screen capture of Tang's VBA script to determine C_s and D_{nss}

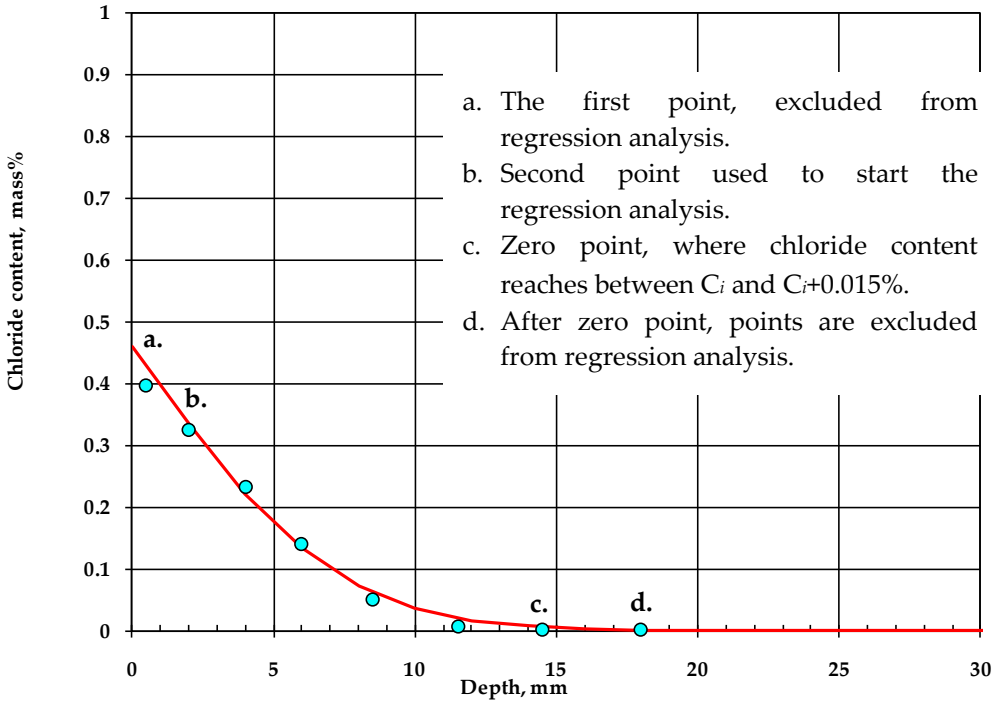


Figure 3.12 Illustration of regression analysis as per CEN TS 12390-11:2010

3.6.2 PD (Potential Difference) test revisited.

Before the beginning of the experimental programme, a small scale research work was started to familiarise the author with all the test methods and to review the candidate test methods for the thesis. An electro-migration chloride test originated in Dundee called the PD test was considered as one of the possible rapid test. The PD test was developed to meet the demand for a test that can rapidly provide a chloride diffusion index (Dhir et al., 1990b).

The PD uses a small potential (10 V) to drive the chloride ions through the concrete specimen in a two-cell arrangement as shown in Figure 3.13. The sample used were 25 mm thick for concrete with nominal aggregate size of 20 mm and 100 mm diameter encased in a diffusion cell with deionised water as anolyte. The use of the large reservoir according to the authors of the test has the advantage of being able to run multi-concurrent tests and preclude chloride depletion in the upstream compartment. The test takes on average two weeks to complete for CEM I concrete. Chloride content is measured by titration of a small quantity (0.5 ml) of the downstream sample against silver nitrate ($AgNO_3$), resulting a reaction that precipitates silver chloride (AgCl) and calculating the chloride amount in parts per million (ppm).

During the review it was found that the 5 molar NaCl solution (177,250 ppm) was observed to be excessive. Although all NaCl was soluble during the preparation time, after several days of migration test, salt started to re-crystallise causing the molarity of the solution to drop. Furthermore the amount of Cl^- transported for the entire duration of the electro migration test rarely exceeds 15,000 ppm. This was observed to happen only twice for very high water-cement ratio (0.7) concrete specimen. As the normal capacity of the test tank with six test running simultaneously is approximately 32 L with only 9 L anolyte (3.6:1 ratio) in the test cell, the amount of chloride migrated is comparatively low (approximately 2.5%) and does not cause significant chloride depletion in the upstream tank. It could be deduced that for the concrete that is tested under this thesis where the highest water-cement ratio is 0.55, the amount of Cl^- migrated will be even lower than 12,000 ppm and that 1 M solution will suffice.

The pH reading was also taken during the PD test. It was observed that the pH value of the downstream solution turns very acidic down to pH 3 within 72 hours of the test. The pH continues to reduce down to pH 1 after about 14 days when the test concludes. Coupled with the reaction from the potential applied, it could be suggested that this environment is too severe for the duration of the test that even the graphite anode used was starting to dissolve after several test runs (Figure 3.14). Therefore the perturbance to the concrete specimen is even greater due to the

high acidity of the downstream solution and a decision was made to abandon the PD test method in favour of the Multi-regime method.

3.6.3 Migration Test – UNE 83987:2009 (Multi-regime)

The Multi-regime test was developed by Andrade, (1993) and subsequently standardised in Spain (UNE, 2009). This was originally developed as a response to the criticised ASTM test developed by David Whiting and addressing the need for a rapid test method to establish chloride diffusion coefficient for concrete. The test uses the classical two cell test set-up with the upstream solution being a 1 M NaCl solution and the downstream solution being distilled deionised water. The arrangement of the cell (see Figure 3.15) meant that the volume amount of upstream and downstream solution (500 ml) is fixed at a ratio of 1:1. The specimen used was 75 mm diameter concrete 25 mm thick cored out of a 100 mm diameter cylinder and cut using a water cooled saw.

Specimen preparation involves vacuum saturation process similar as described in the immersion test. The specimens, after approximately 18 hours of immersion, were transferred directly to the test cell for the Multi-regime test that runs for approximately 2 weeks. The anolyte solution for the test is distilled deionised water and the catholyte solution 1 M NaCl. The cell when assembled was weighed first empty then weighed with distilled deionised water and with NaCl to determine the volume of each solution. Specimens were tested in triplicates.

At the start of the test and throughout the test duration, conductivity of the anolyte solution was checked using a calibrated conductivity meter. Calibration of the meter was done every week to ensure correct reading of the conductivity. Voltage passed between the two faces of the specimen was also measured. The conductivity and voltage readings were made every 24 hours until steady state flow has been established and started to move into an asymptote. This signals the test being completed. Figure 3.16 shows the measurement of voltage and conductivity on the test cells. Selectively pH measurements were made and it was observed that the pH of different cement subjected to the migration test differs between pH 10 and pH 4. This is undoubtedly better in comparison to the PD test method that causes very low pH values that could possibly perturb the specimen during testing. Results are discussed in Chapter 6.

The conductivity measurements were entered into a spreadsheet application to calculate the D_{ssm} value in accordance to the modified Nernst-Planck equation. It was reported by RILEM technical committee (TC 178-TMC) that the multi-regime test has a percentage of average bias of 10% from the target value and repeatability and reproducibility of 22% and 69% respectively (Castellote et al., 2006).

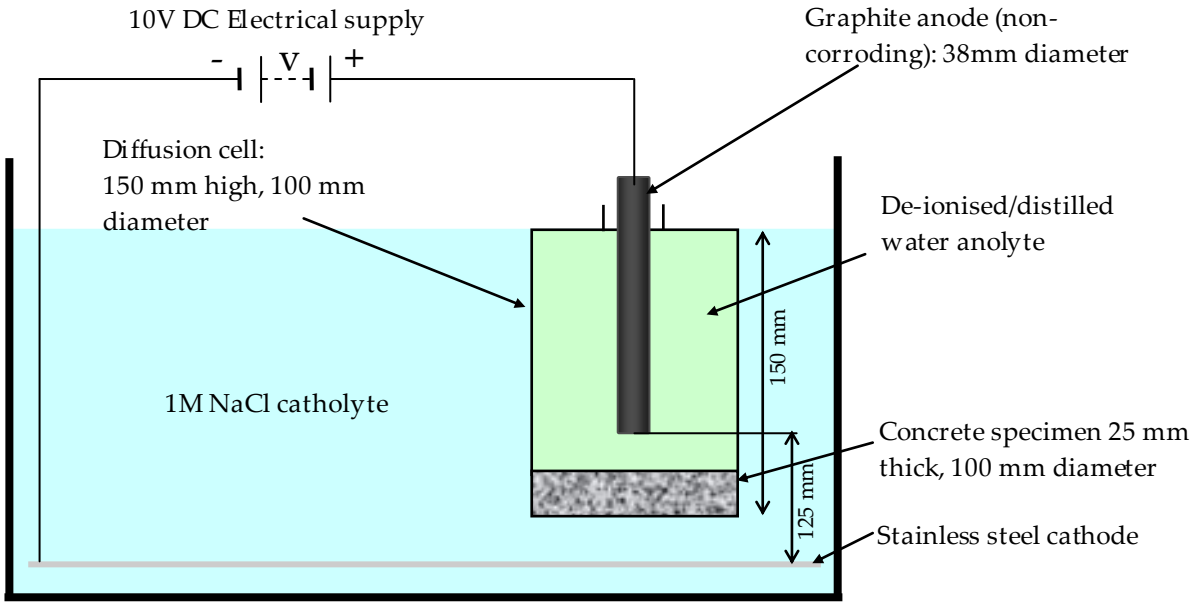


Figure 3.13 Schematic representation of PD test

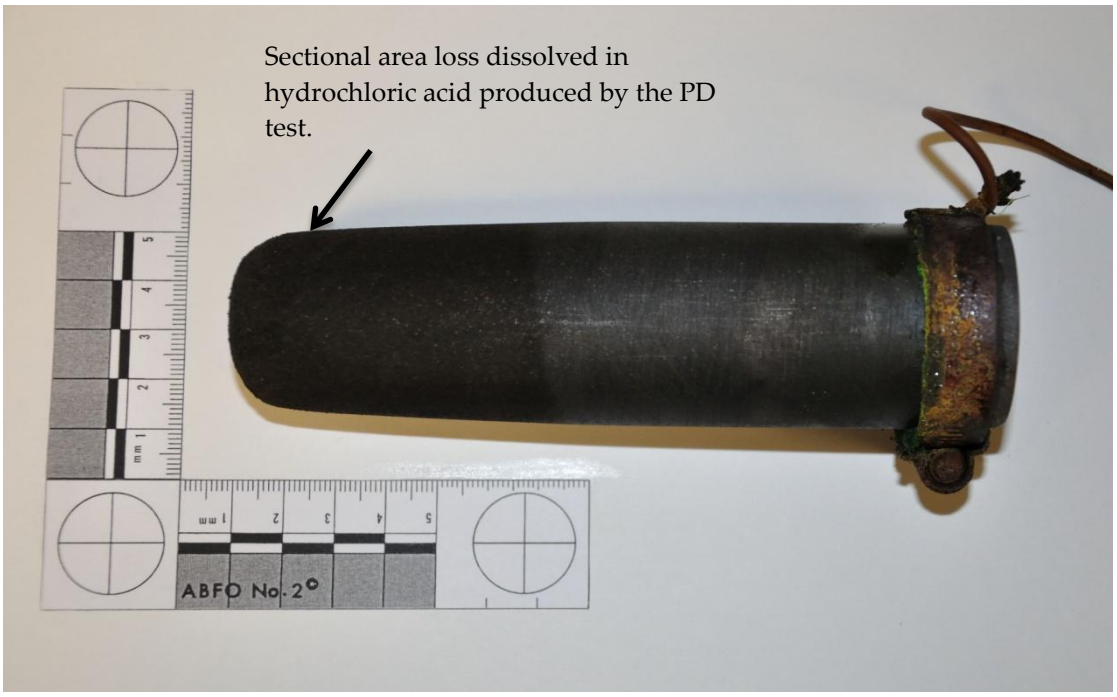


Figure 3.14 Graphite anode used in the test. Note: Originally the end is cylindrical

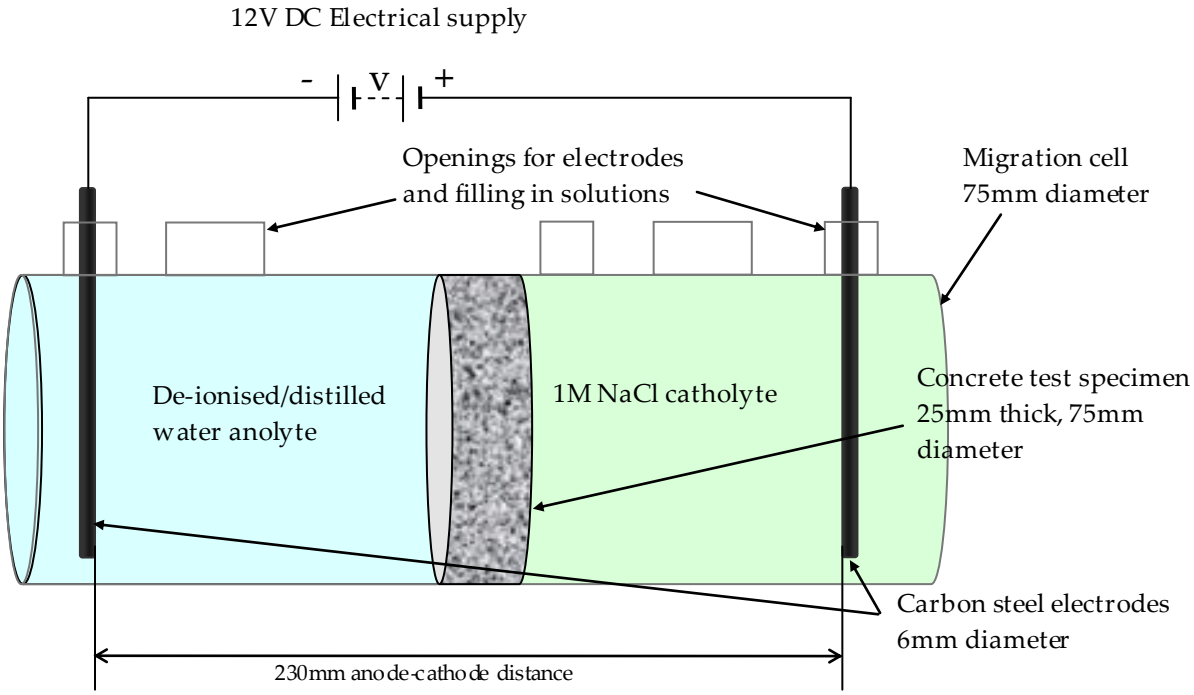
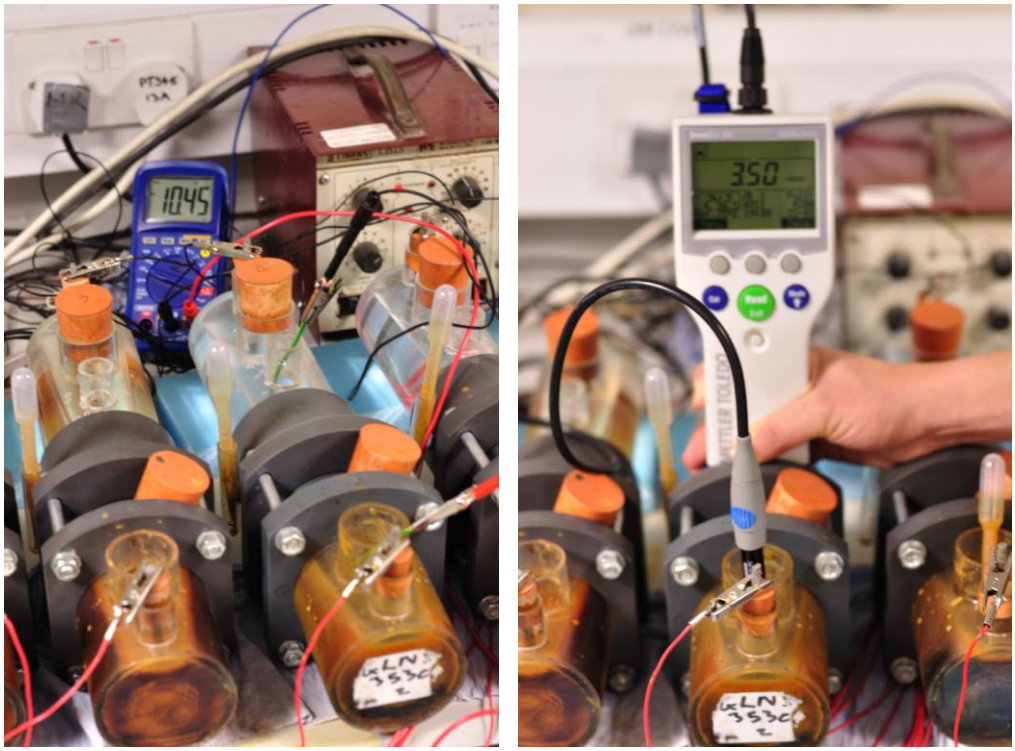


Figure 3.15 Schematic representation of UNE 83987:2009 (Multi-regime) test



i. Measurement of voltage drop across the specimen

ii. Measurement of conductivity

Figure 3.16 Procedure for Multi-regime test

3.6.4 Migration Test- NT Build 492

NT Build 492 measures the non-steady state diffusion coefficient. This is a standard test adopted in the Nordic countries. The test uses the electro-migration principle to drive chloride ion through 100 mm diameter 50 mm thick concrete disc. Specimens are initially cut using water cooled saw to the required thickness before being vacuum saturated. The vacuum saturation procedure for NT Build 492 is slightly different to other tests described earlier in that after 3 hours of vacuum, the specimens were saturated with saturated calcium hydroxide $Ca(OH)_2$ solution for 1 hour before stopping the vacuum pump. Saturated $Ca(OH)_2$ solution were prepared by dissolving more than 1.6 gm of $Ca(OH)_2$ per litre of water. The specimens were left in the saturated solution for 18±2 hours before testing began. After 18±2 hours and if the specimens were not yet tested, they were taken out and put in a close fitting sealed plastic bag and stored in a > 96% RH chamber at 20 - 25 °C until the time of testing.

Testing involved fitting the specimens in a rubber sleeve and then clamping to secure it against leaking. Additionally the circumferences inside the rubber sleeve are coated with a thin layer of silicone grease to ensure water tightness. This allows for the specimens to be kept wet throughout the preparation period before the commencement of the NT build test. Catholyte solution used is 10% NaCl solution and the anolyte 0.3 M sodium hydroxide (NaOH). The test runs between 24 hours and 96 hours depending on the initial current observed for 30 V preset in the beginning and then adjusting to the proposed initial current and voltage as given in the standard. Figure 3.17 shows the schematic of the NT Build 492 test method.

At the end of the test, the anolyte solution temperature and the final current were recorded before removing the specimen from the rubber sleeve and splitting open. 0.1 M $AgNO_3$ solution is then sprayed to the split surface to induce a chemical reaction between chloride in the specimen and silver in the solution to precipitate silver chloride.

It was observed that sometimes the indication for the colorimetric test was not easy to be determined and in a number of occasions, no colour change boundary can be observed confidently. Tests with flouresceine indicator as used by Collepardi was tried to more clearly visualise the colour change boundary. This method involves spraying a flouresceine solution – made with 1 gm per litre flouresceine in 70% ethylic alcohol – to the split surface prior to the 0.1 M $AgNO_3$ solution. This reveals as a dark-pink hue on the chloride contaminate zone and a black chloride free zone. However, it was found that this method was less effective in revealing the colour change boundary compared to spraying with only 0.1 M $AgNO_3$ solution.

During testing it was also observed that when 0.1 M $AgNO_3$ solution was sprayed and the specimens were left indoors under artificial light to dry, the precipitates turned grey/white as shown in Figure 3.18. The chloride free area turns brown. However, when the specimens are left to dry in outside air, the precipitates turns dark. It was decided to stick with the former method with the specimen drying indoors after spraying instead of outdoors as the colour change boundary was more pronounced by comparison. Specimens were tested in duplicates, where each specimens was split into two and the average of measurements from four sides taken. The accuracy of the measurement is given in mm following the recommendation of Baroghel-Bouny, (2007a).

The RILEM TC 178-TMC reported the average percentage bias of this test to its target value as 20%, and the reproducibility and repeatability as 36% and 18% respectively (Castellote et al., 2006). However, later in a European round robin test conducted in the European project Chlortest the repeatability and reproducibility COV of this method were reported to be 15.2% and 23.6%, respectively (Tang and Basheer, 2007).

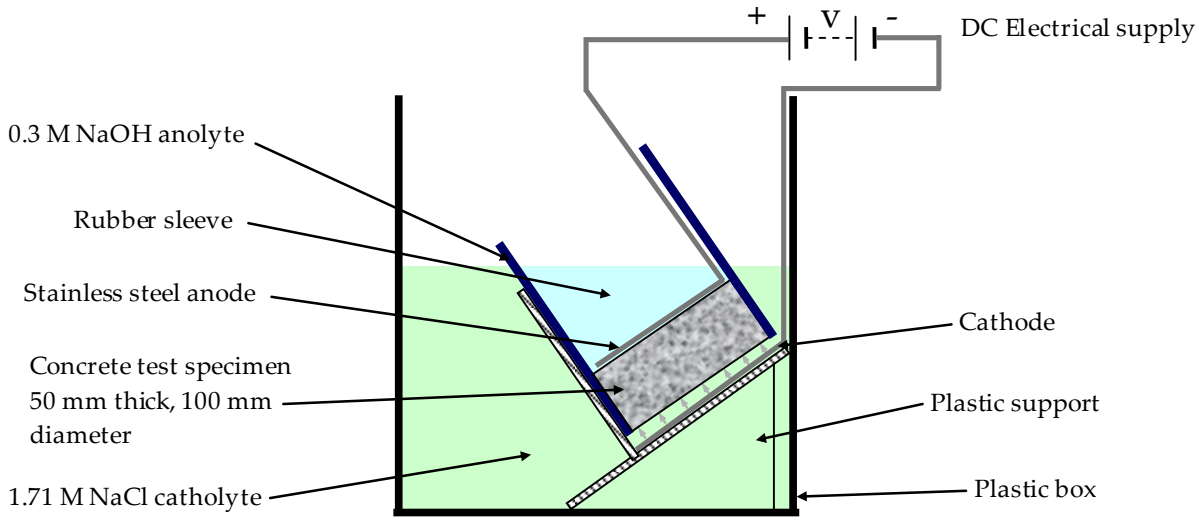


Figure 3.17 Schematic representation of NT Build 492 test

i. Spraying 0.1 M $AgNO_3$ on the specimen after splitting

ii. Typical colour change boundary after spraying

Figure 3.18 NT Build 492 measurement procedure

3.6.5 Wetting and drying conditions

Tidal, splash and spray zones are considered to be the most severe of the exposure environments and classed as XS3 in the BS 8500-1:2006 (BSI, 2006a). This area is affected by a number of physical actions that can drive chloride further into the concrete than any other exposure environment. It was also shown that sulfate in seawater alters the binding characteristic of chloride in concrete (Zibara, 2001). This test is designed to simulate this condition in the lab, where the specimens are put into a wetting and drying cycle similar to those of the sea water environment.

Soluble sea salt for aquarium was used to simulate this condition. The composition of the salt solution for the tidal cycle is based on the standard mean seawater composition. This is marginally higher than the North Sea composition as the North Sea is fed by a number of tributary rivers along the European and English coast. The dry salt comes in a pre-mixed container and added to potable tap water to make up the solution. However, the concentration of the solution was modified to a factor of 1 M NaCl. Table 3.17 shows the exposure solution composition as compared to the typical North Sea composition.

The natural seawater concentration is 0.546 mol/kg. By increasing the molar concentration of NaCl by a factor of 1, the concentrations of other ions are increased proportionately. The reason this was done is to accelerate the ingress of chloride ions as the concrete specimens were not submerged continuously. It was also speculated that with higher concentration, the precipitation of brucite in the surface of the specimens can be intensified. As a result, the possible pore blocking skin effect can be investigated.

Specimens were placed in the tank after the 28 days wet curing period. All but one side were then coated with paraffin wax and then cling wrapped to allow for a uniaxial ingress of the exposure solution. The specimens were then arranged face-up in the tidal tank facing the blower to maximise drying on the surface of the specimens during the drying cycle.

Period of cycle is determined at six hours dry and six hours wet according to the time of the day. The solution was topped up regularly, every 2 – 3 weeks to replace fluids lost by evaporation and leakage of the reservoir tank.

Table 3.17 Molar composition of ions in seawater vs Instant Ocean salt mix (mol/kg solution)

Ion	[a)]Instant Ocean Sea Salt	[b)]Typical North Sea ion concentration	[c)]Salt solution for cyclic wetting and drying exposure
Chloride (Cl^-)	.521	0.54586	1.0
Sodium (Na^+)	.462	0.46906	.817
Sulfate (SO_4^{2-})	.023	0.02824	.044
Magnesium (Mg^{2+})	.052	0.05282	.010
Potassium (K^+)	.0094	0.01021	.018
Calcium (Ca^{2+})	.0094	0.01028	.018
Carbonate/bicarbonate (CO_3^{2-})	.0013	0.00026	.002
Bromide (Br^-)	-	0.00084	-
Strontium (Sr^{2+})	.00019	0.00009	.0003
Hydroxide (OH^-)	-	0.00001	-
Fluoride (F^-)	-	0.00007	-
Boric Acid ($B(OH)^3$)	-	0.00032	-
Carbon Dioxide (CO_2^*)	.0013	0.00001	.002
Hydrogen Carbonate (HCO_3^-)	.00165	0.00177	.003
$(B(OH)_4^-)$	-	0.00010	-

[a)] Atkinson and Bingman, (1997)
[b)] Dickson et al., (1988)
[c)] conversion factor calculated as: a) × 1.9193
[(-)] not reported

The exposure tanks have been developed for an earlier PhD work done in the University of Dundee in 1997 by Henderson (1997). The uPVC tanks allow for many specimens to be exposed at one time and consist of a main tank that holds the specimens and a storage tank that holds the exposure solution during the drying cycle. Dimension of the main tank is 800 mm × 800 mm × 610 mm high internally. The storage tank measures 900 mm × 900 mm × 300 mm and can hold approximately 210 l of solution. The main tank is fed with the exposure solution stored in the storage tank via a non-corrosive pump in the wetting cycle and gravity returned to the storage tank during the drying cycle. Figure 3.19 shows the schematic of the cyclic wetting tidal tank (Figure 3.20) used in the project.

3.6.6 Highway exposure

The specimens for highway exposure (XD exposure class) was neither waxed nor cut as the specimens for the CEN test. This is to allow for natural exposure to take place.

The specimens were then placed at Dundee University's highway exposure site off highway A928 near Glamis Castle, Angus. This road was identified as the most severe site in the UK for freezing and thawing cycles especially at the exposure site. Consequently the road is heavily salted by the local authority. Figure 3.21 and Figure 3.22 shows the specimens at the exposure site.

3.6.7 Preparation of solutions

Some of the chemical solutions for testing are made in the laboratory. Salts used for the exposure solutions are bought in from suppliers with the purity of 99.9% and mixed using either tap water or deionised water depending on the described test procedures. Deionised water was obtained by filtration of mains tap water with disposable deioniser cartridges.

Standard preparations such as 0.1 M $AgNO_3$ are available commercially so this and other standard solutions are bought instead of being mixed in the laboratory.

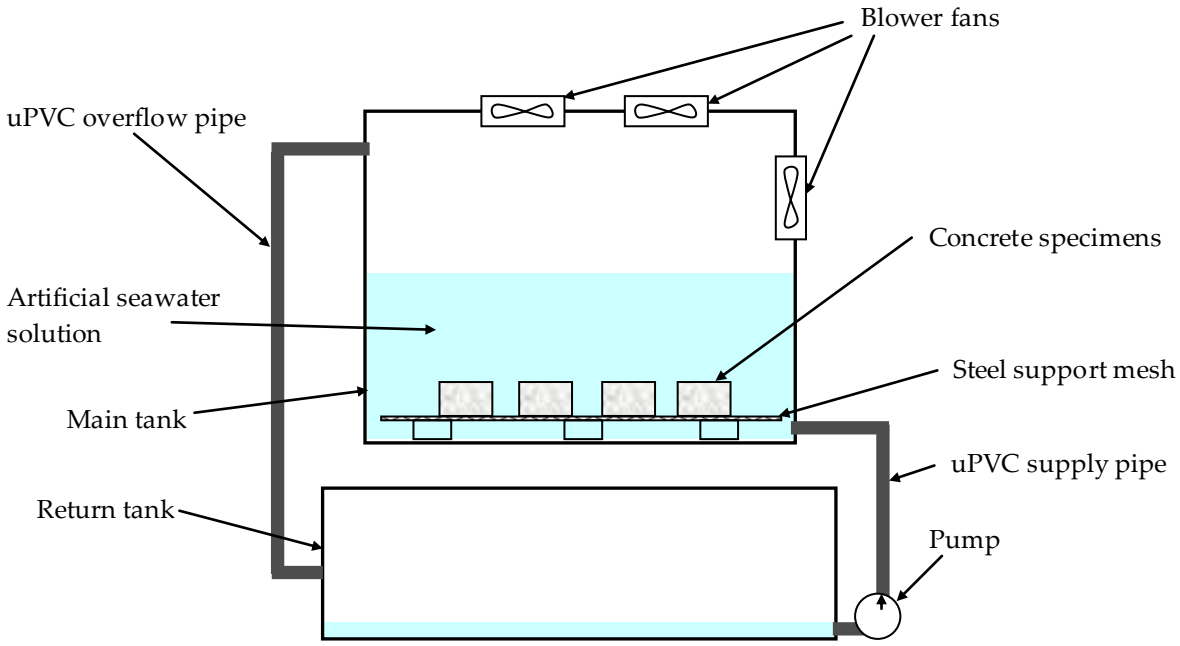


Figure 3.19 Schematic representation of the cyclic wetting tank

Figure 3.20 Cyclic wetting and drying tank used for the study

Figure 3.21 Highway specimens

Specimens for the highway exposure to be retrieved after several winter seasons

Figure 3.22 Highway specimens are placed behind the Armco barrier exposed to winter de-icing

3.6.8 Investigations by research group

In addition to the main test procedures, there were several MSc research projects that were affiliated to, and co-supervised by the author. The students were tasked to investigate certain aspects of the CEN TS 12390-11:2010 test methodology, namely comparison between the 3 allowable exposure methods as well as brucite precipitation in cyclic wetting exposure and possible artefacts of the steady-state UNE 83987:2009 migration test. The results of these studies provide a better picture with respect to the performance of chloride with the different test methods. The title of their thesis's and the description of their work are described below.

3.6.8.1 Performance of Concrete in Chloride Environments: Comparison of Performance Test Methods

This study compares the D_{nss} value measured from the immersion, ponding and inversion exposure listed in the CEN TS 12390-11:2010. The mix proportion for this study uses the same cement source as the main study but a different type of aggregate. Magnesian limestone was used in two size grades, 4/10 mm and 10/20 mm. Normal local sand was used as fine aggregate, the same kind used in the main thesis work. The coarse aggregates used were characterised as hard, angular, and has an absorption rate of 1.3% for the 10/20 mm and 1.5% for 4/10 mm. The mix proportions and the 28 days compressive strengths are detailed in Table 3.18.

There are concerns of allowing 3 test procedures for a single test method as there may be artefacts that can influence the result of different procedures. The test methodology was followed as detailed in the technical specification but the inversion test was done at a lower surface area to solution volume ratio than what is recommended. Minimum solution volume per cm^2 area was 12.5 ml/cm^2 and this was followed for ponding and immersion test whilst the inversion test in this project uses only about 4 ml/cm^2. The author has recalculated the D_{nss} values using the raw data generated by the student.

3.6.8.2 Effect of Leaching and Ageing on Rapid Chloride Migration Test

Concrete specimens are normally cured in water for at least 28 days before any laboratory tests are performed on them. With respect to two-cell migration test methods, specimens are also vacuum saturated with deionised water and left to soak in them for 24 hours before the tests can begin. Since leaching of portlandite can occur in these conditions, there is an interest to investigate whether leaching of portlandite can affect the results of the measurements.

This investigation studied the effect of ageing and leaching on the PD test, a steady-state migration test designed at the University of Dundee (Dhir et al., 1990b) and Multi-regime test, (UNE 83987:2009) (Castellote et al., 2001b). The study involves immersing 25 mm thick by 100 mm diameter test specimens in deionised water that was renewed every 48 hours for 28 and 56 days after 90 days of normal curing. After the specified leaching period, powder samples were collected from the surface and the middle of the samples. The samples were scanned with XRD to determine the difference in the mass of Portlandite. This study uses the same concrete mix as the study above.

To study the effect of the leaching procedure on the D_{ssm} value obtained, PD and Multi-regime test were conducted on the un-leached specimens at 28 and 90 days. Leached specimens were tested at 120 and 150 days.

3.6.8.3 Effect of Brucite on Chloride Ingress

This study investigates the effect of exposure to cyclic wetting and drying of concrete specimens exposed to sodium chloride (NaCl) and magnesium chloride ($MgCl_2$). It was intended to compare the rate of chloride diffusion in systems where chloride diffusion is un-inhibited (NaCl) and inhibited ($MgCl_2$) due to the possible pore blocking effect of brucite precipitation on the concrete skin. This study too uses the same cement materials as the main thesis and it uses the Magnesian limestone aggregates in 2 size fractions as the previous 2 studies. The mix proportions and the 28 days compressive strengths are detailed in Table 3.19.

It is a popular view that there is a surface skin effect when the rate of chloride diffusion from seawater exposure is considerably slower than chloride diffusion in pure NaCl exposure. This was believed as a result of brucite ($Mg(OH)_2$) precipitation on the surface of concrete resulting from the reaction of magnesium salts in seawater with $Ca(OH)_2$ that acts as a pore blocker. The test programme was designed to test the rate of chloride diffusion in cyclic wetting using NaCl exposure and $MgCl_2$ exposure. Due to the different ionic structure, and the need to keep the concentration of the chloride ion the same, the NaCl solution was made up as 2 M/litre whilst $MgCl_2$ solution is made up as 1 M/litre. The wetting and drying cycle was set at 5 hours wetting and 3 hours drying and the period of exposure was 90 days.

Table 3.18 Mix proportions for comparison of performance test and effects of leaching projects

Mix code	EN 197 notation	Constituent Proportions (kg/m³)											Achieved strength, N/mm² @ 28 days
		w/c	Free Water L/m³	Cements/additions						Aggregates			
				PC	GGBS	Fly Ash	Silica Fume	Limestone	Total Cement	Fine	4/10 mm	10/20 mm	
C1	CEM I 52,5 R	0.35	135	380	-	-	-	-	380	735	405	745	72.5
C2	CEM I 52,5 R	0.40	150	380	-	-	-	-	380	730	400	740	69.5
C3	CEM I 52,5 R	0.45	160	360	-	-	-	-	360	735	400	745	54.5
C4	CII/B-V	0.35	135	265	-	115	-	-	380	715	390	730	53.0
C5	CII/B-V	0.45	160	250	-	110	-	-	360	715	390	725	41.0
C6	CII/B-V	0.55	180	225	-	95	-	10	330	705	395	735	26.5
C7	CIII/B	0.40	150	115	265	-	-	-	380	725	400	735	49.5
C8	CIII/B	0.50	170	100	240	-	-	-	340	735	400	745	50.5
C9	CIII/B	0.55	180	95	225	-	-	10	330	725	405	750	28.0
C10	CII/A-LL	0.35	135	325	-	-	-	55	380	735	400	750	81.5
C11	CII/A-LL	0.40	150	325	-	-	-	55	380	730	400	740	66.5
C12	CII/A-LL	0.50	180	306	-	-	-	54	360	732	401	745	55.5

Table 3.19 Mix proportions for effects of brucite project

Mix code	EN 197 notation	Constituent Proportions (kg/m³)											Achieved strength, N/mm² @ 28 days
		w/c	Free Water L/m³	Cements/additions						Aggregates			
				PC	GGBS	Fly Ash	Silica Fume	Limestone	Total Cement	Fine	4/10 mm	10/20 mm	
A1	CIV/B-V	0.40	150	230	-	150	-	-	380	765	370	685	58.0
A2	CIV/B-V	0.45	160	215	-	145	-	-	360	770	370	690	53.5
A3	CIV/B-V	0.50	170	205	-	135	-	-	340	775	375	690	47.0
A4	CIII/A	0.35	135	135	245	-	-	-	380	790	380	705	68.5
A5	CIII/A	0.45	160	125	235	-	-	-	360	785	380	705	68.0
A6	CIII/A	0.55	180	110	210	-	-	10	330	780	385	715	37.5
A7	CII/A-D	0.35	135	355	-	-	25	-	380	795	385	705	79.5
A8	CII/A-D	0.40	150	355	-	-	25	-	380	785	380	705	93.5
A9	CII/A-D	0.55	195	355	-	-	25	-	360	775	375	695	73.0
A10	CII/A-LL	0.35	135	325	-	-	-	55	380	795	385	705	80.0
A11	CII/A-LL	0.40	150	325	-	-	-	55	380	785	380	705	69.5
A12	CII/A-LL	0.45	160	325	-	-	-	55	360	790	380	710	69.5

CHAPTER 4. DIFFUSION COEFFICIENT BENCHMARK USING THE CEN TS 12390-11:2010 TEST METHOD FOR XD3 AND XS3 EXPOSURE CLASSES CONCRETE IN BS 8500-1:2006

4.1 INTRODUCTION

The background to this project is to first determine the baseline diffusion coefficient value for typical concrete at the limit of BS 8500-1:2006. This will enable the evaluation of the chloride resistance performance offered by the current standard based on the prescriptive-based limiting values approach. BS 8500-1:2006 controls the minimum compressive strength, maximum water-cement ratio and the minimum cement or combination content for concrete. The provisions in BS 8500-1:2006 with regards to maximum water-cement ratio for XD and XS exposure are different than the provisions recommended in BS EN 206-1:2000.

The concern of BSI with BS EN 206-1:2000 was that there is no proper separation between different cements on the main standard. The rationale was, it is known that cement properties, chemically and physically are different and these differences influence the ingress of chloride. BS 8500-1:2006 was written to address this concern and give engineers better guidance as to the framework for durability design in chloride environment.

Adherence to these control parameters suggest that the concrete specifiers and producers have conformed to the desired durability requirement of a concrete structure to the intended service life of either 50 years or 100 years. The approach of BS 8500-1:2006 suggests that mixes conforming to the limiting values of compressive strength, maximum water-cement ratio and minimum cement or combination content may achieve satisfactory resistance with regard to chloride ingress.

Cement/combination types are separated into three different bands diverging from the approach of BS EN 206-1:2000. CEM I, II/A, II/B-S and SRPC in the first group, II/B-V and III/A in the second group and III/B and IV/B-V in the last group in order of perceived resistance to chloride from lowest to highest. Table 4.1 shows the limiting values for each group for XD3 and XS3 exposure environment. Table 4.2 shows the limiting values for XD3 and XS3 in BS EN 206-1:2000.

Due to sustainability pressures, the concrete industry is also being pushed to reduce CO_2 emission contributed largely by manufacturing Portland cement. With regards to chloride durability, it has been shown that Portland cement clinker replacement with other constituent elements especially pozzolanic and/or ultra-fine materials are beneficial in reducing chloride ingress. CEN member

countries through BS EN-206-1:2000 and BS EN-197-1:2000 are presented with 27 different cement products that can be selected to any specific environment.

The move from prescriptive-based specification to performance specification requires an accepted test methodology to establish performance. Although there are many test methods proposed, and some have even been standardised in several countries, so far there is no accepted universal test method to fundamentally establish performance and benchmark durability. CEN TC 51(CEN TC 104)/ WG12/TG/5 is tasked to assess and propose a chloride diffusion test at the European level.

The work is directed by the view that the concretes specified on prescriptive-based specification based on the limiting values of BS 8500-1:2006 are significantly different in their chloride resistance performance.

The results of the tests within the period of one year for XD and XS exposure environment for the intended service life of 100 years are presented here.

4.1.1 Age at test

Due to the number of mixes considered and the research commitments, not all tests started at the same age. This would be the ideal case. It has also been acknowledged that mixes with pozzolanic materials such as fly ash and blastfurnace slag do not achieve their optimal durability until a later age(Bleszynski et al., 2002, Nokken et al., 2006a). Expert opinion differs in this matter as to the ideal age to which durability comparison be made, with ages of up to 90 days and maybe more are suggested to make a fair comparison. This knowledge is balanced with the practical needs of engineering practices to know as early as possible the quality and performance of a candidate concrete design within the equivalent durability framework.

In order to make a fair comparison between cements on the basis of equal strength and water-cement ratio, data from the different test ages were interpolated. The measurement data from this experimental programme allows for the interpolation for age comparison between 20 weeks to 52 weeks (almost five months to one year) as some of the concrete specimens were not tested earlier than 20 weeks.

4.1.2 Reference concrete

As far as the author is aware , there is no concrete mix that is being regarded as a benchmark mix for the UK. However, based on discussions with the first supervisor and consideration of the literature, a benchmark mix is ideally a mix that uses either 30% fly ash or 50% ggbs with minimum 50 N/mm^2 compressive strength at 28 days and designed for 50 mm minimum cover.

Table 4.1 Durability recommendation for reinforced or prestressed elements with an intended working life of at least 100 years in BS 8500-1:2006 (BSI, 2006a).

Nominal cover	Compressive strength class where recommended, maximum water-cement ratio and minimum cement or combination content for normal weight concrete with 20 mm maximum aggregate size					Cement/combination types
mm	45 + Δc	50 + Δc	55 + Δc	60 + Δc	65 + Δc	
XD3	–	–	C45/55 0.35 380	C40/50 0.40 380	C35/45 0.45/ 360	CEM I, II/A, II/B-S, SRPC
	C40/50 0.35 380	C35/45 0.40 380	C32/40 0.45/ 360	C28/35 0.50/ 340	C25/30 0.55 320	II/B-V, III/A
	C32/40 0.40 380	C28/35 0.45/ 360	C25/30 0.55 340	C25/30 0.55 320	C25/30 0.55 320	III/B, IV/B-V
XS3	–	–	–	C45/55 0.35 380	C40/50 0.40 380	CEM I, II/A, II/B-S, SRPC
	C40/50 0.35 380	C35/45 0.40 380	C32/40 0.45/ 360	C28/35 0.50/ 340	C25/30 0.55 320	II/B-V, III/A
	C32/40 0.40 380	C28/35 0.45/ 360	C25/30 0.55 340	C25/30 0.55 340	C25/30 0.55 340	III/B, IV/B-V
A dash (−) indicates that greater cover is recommended						

Table 4.2 Recommended limiting values for composition and properties of concrete in BS EN 206-1 (BSI, 2000b)

	Exposure classes	
	XD3	XS3
Maximum w/c	0.45	0.45
Minimum strength class, N/mm^2	C35/45	C35/45
Minimum cement content, kg/m^3	340	340

This is based on factors of performance, material availability, workability, low carbon footprint materials and striking a balance between construction costs and other durability risks, particularly carbonation.

The target strength for the fly ash and ggbs mixes in this thesis is between 30 N/mm^2 to 35 N/mm^2 but 0.50 water-cement ratio 50% ggbs mix (CIII/A) is more realistic for the purpose of reference as can be seen in its performance later in this chapter.

4.2 PERFORMANCE AT ALL AGES

Figure 4.1 to Figure 4.6 give the non steady-state D values (D_{nss}) based on CEN TS 12390-11:2010 for all concrete at their respective time of testing. Data presented are the average D_{nss} values from a maximum of three test cubes. Outliers are determined visually by observation of the overall data especially regression trends and the expected behaviour. These outliers were excluded from the calculation of the average value presentation. Raw data showing each measured data points are included in APPENDIX E.

Figure 4.1 and Figure 4.2 show all mixes, cast following maximum water-cement ratio and minimum cement/combination types requirement of BS 8500-1:2006 and the results of CEN TS 12390-11:2010 of these mixes tested at several ages. Several mixes were expected to not achieve target strength and they were re-cast with a lower water-cement ratio. They are coded as S2 mixes.

It can be seen that below 5×10^{-12} m^2/s the diffusion coefficient values does not change significantly with age. Above 5×10^{-12} m^2/s, the reduction (and occasional increase) of diffusion coefficient values can be seen clearly. These raw results also show that at early age fly ash mixes are severely disadvantaged compared to other cements although the rate of improvement for diffusion resistance is higher than other cements.

It is the author's belief that the 7 weeks measurement for 0.4 water-cement ratio CEM I in Figure 4.1 is not reflective of the expected performance which is expected to be around 20×10^{12} m^2/s. This is based on the observed value for 0.35 water-cement ratio CEM I in Figure 4.2 (in the region of 15×10^{-12} m^2/s at the early age) as well as D value measurements from other test methods to be described in later chapters. Normalisation of the D_{nss} value for Equivalent Durability Performance for CEM I cements in Section 4.3 therefore excludes this point and a hypothesised linear trend is proposed from the 2 remaining points.

4.2.1 Performance at 20 weeks[1]

Figure 4.3 and Figure 4.4 shows the interpolated performance of mixes at 20 weeks equal age for XD3 and XS3 exposure respectively.

4.2.2 Performance at 50 weeks

Figure 4.5 and Figure 4.6 shows the interpolated performance of mixes at 20 weeks equal age for XD3 and XS3 exposure respectively.

[1] The 20 weeks and the subsequent 50 weeks performance in this and subsequent chapters, refers to the actual age of the concrete specimens at the start of the test. That is from casting date, including the 28 days curing, up to the date of the test commencement. The period of the test of 90 days was not counted as part of the concrete age. This follows the specification described in CEN TS 12390-11:2010.

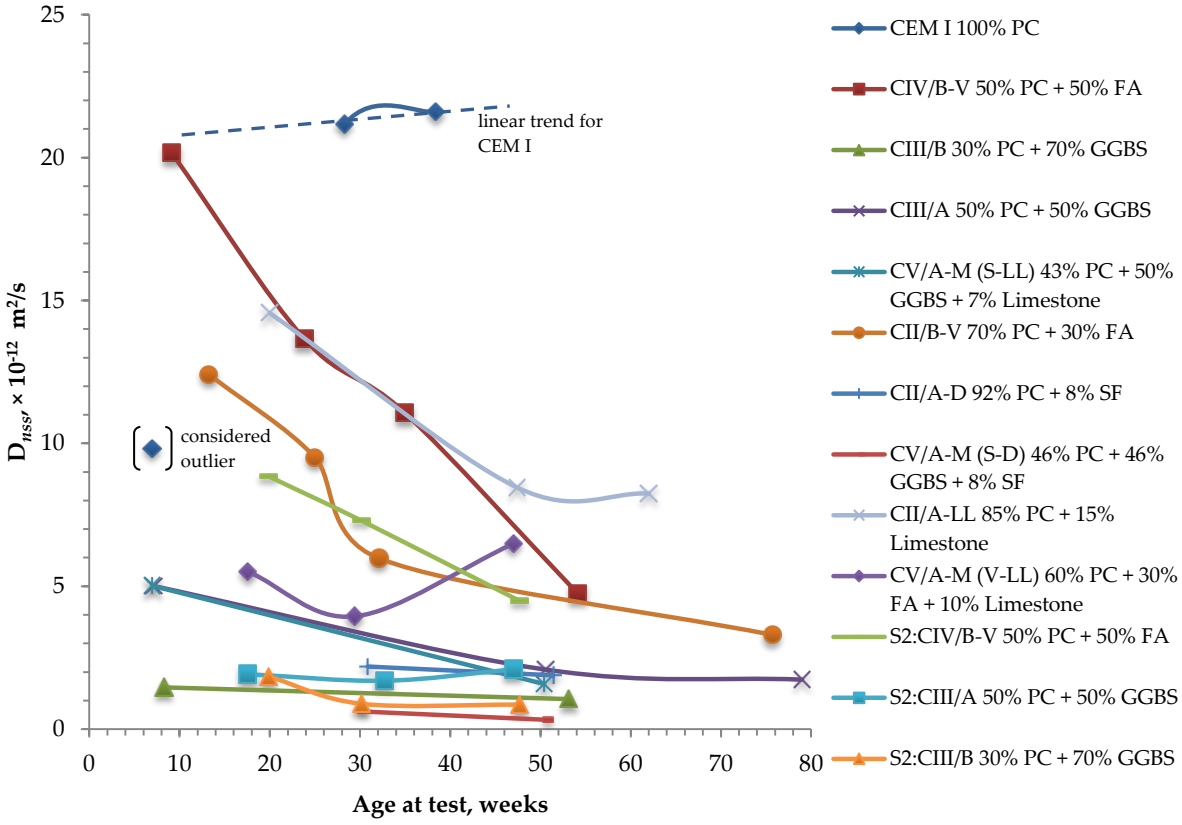


Figure 4.1 **Measured CEN TS12390-11 D_{nss} values for XD3 class concretes**

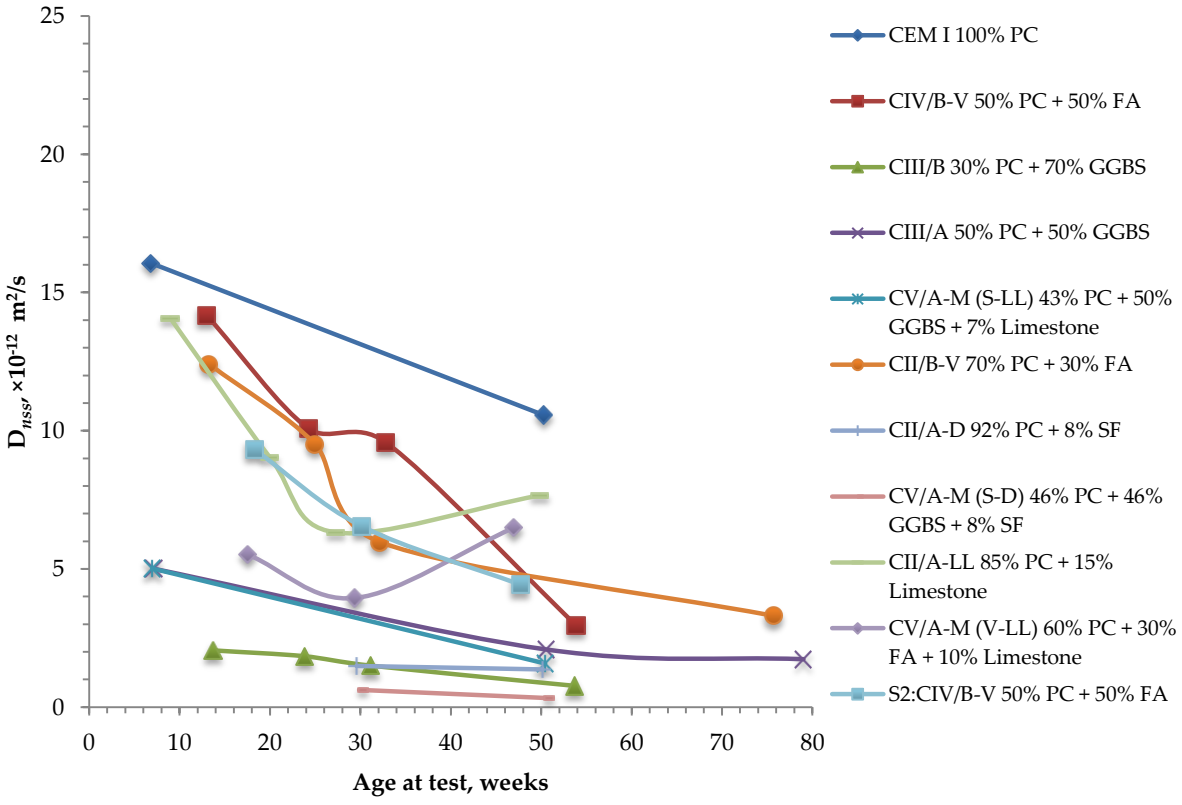


Figure 4.2 **Measured CEN TS 12390-11:2010 D_{nss} values for XS3 class concretes**

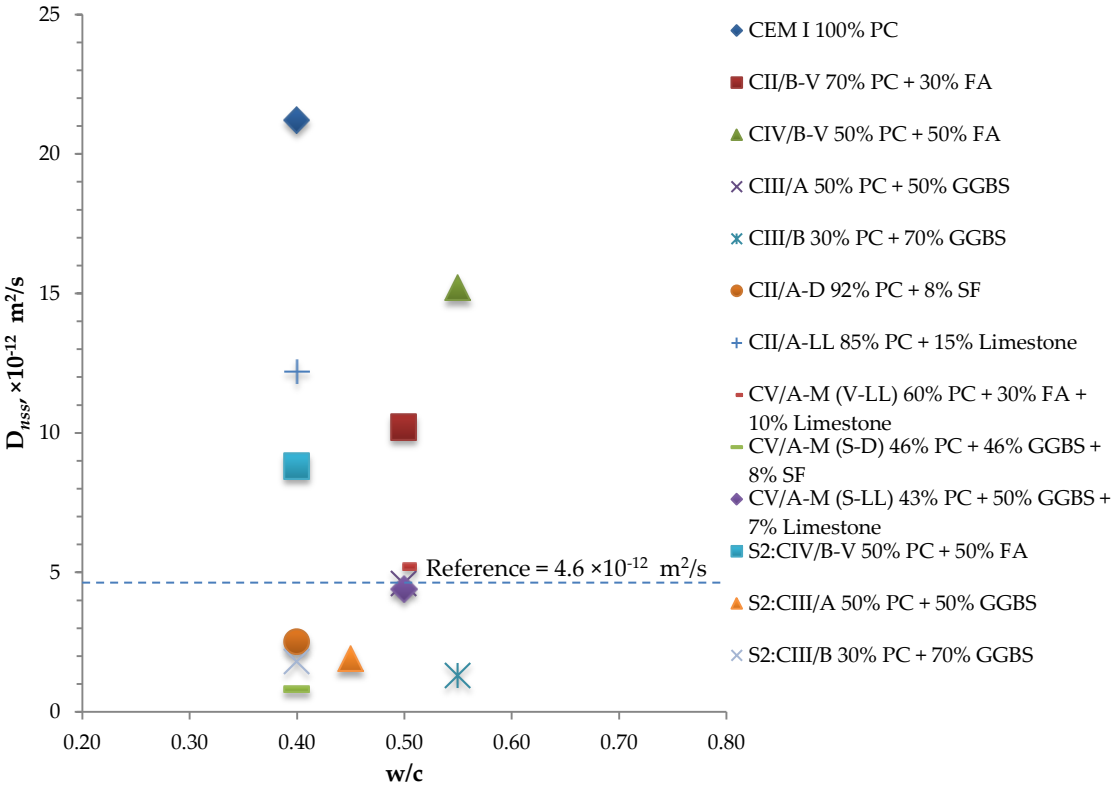


Figure 4.3 **Performance of 20 weeks XD3 class concrete, CEN TS 12390-11:2010**

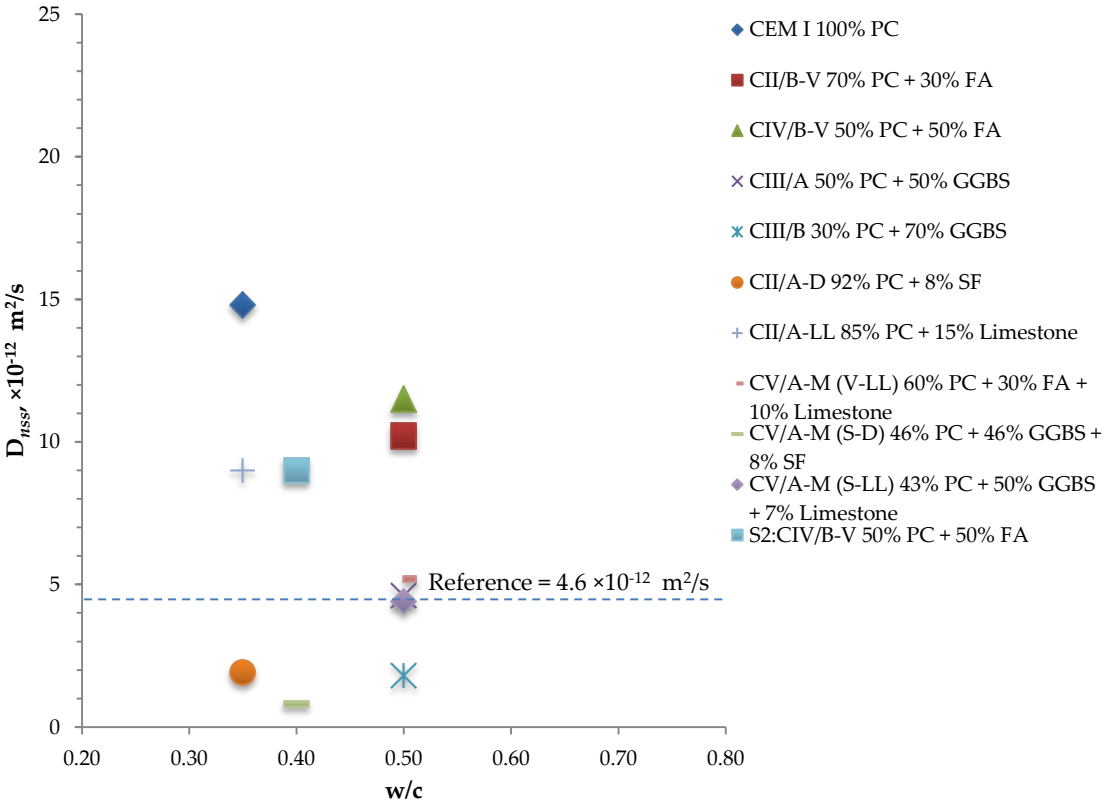


Figure 4.4 **Performance of 20 weeks XS3 class concrete, CEN TS 12390-11:2010**

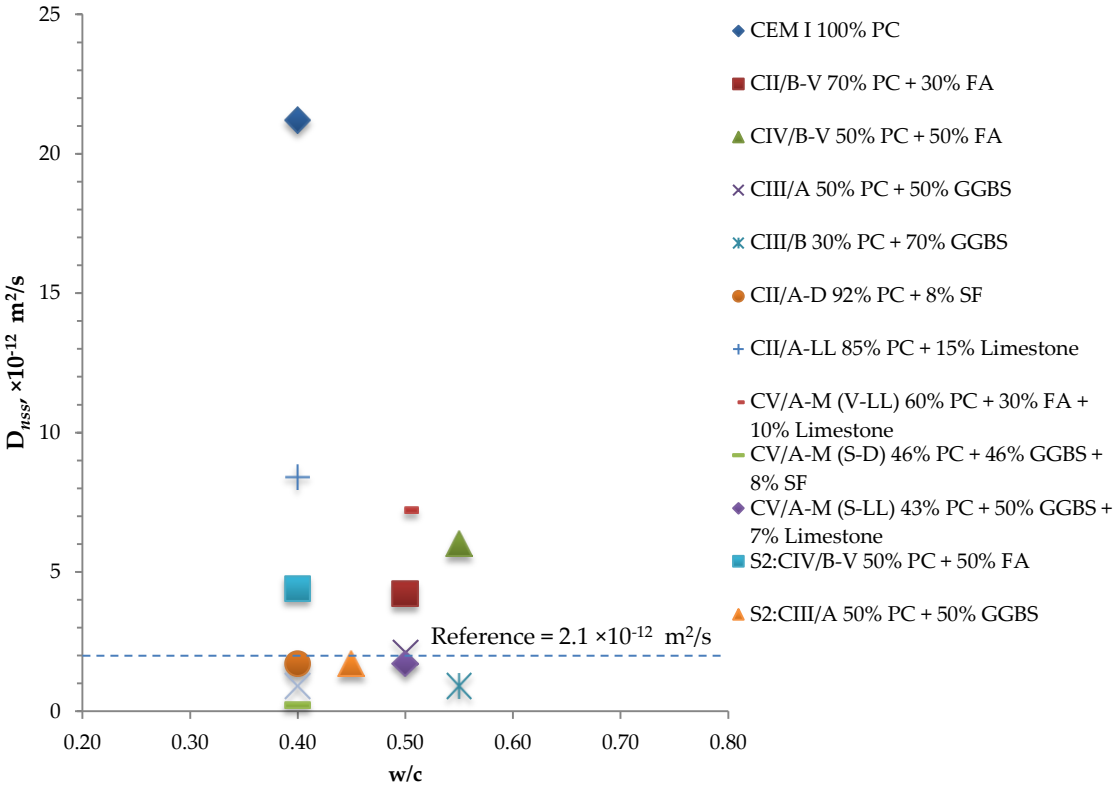


Figure 4.5 **Performance of 50 weeks XD3 class concrete, CEN TS 12390-11:2010**

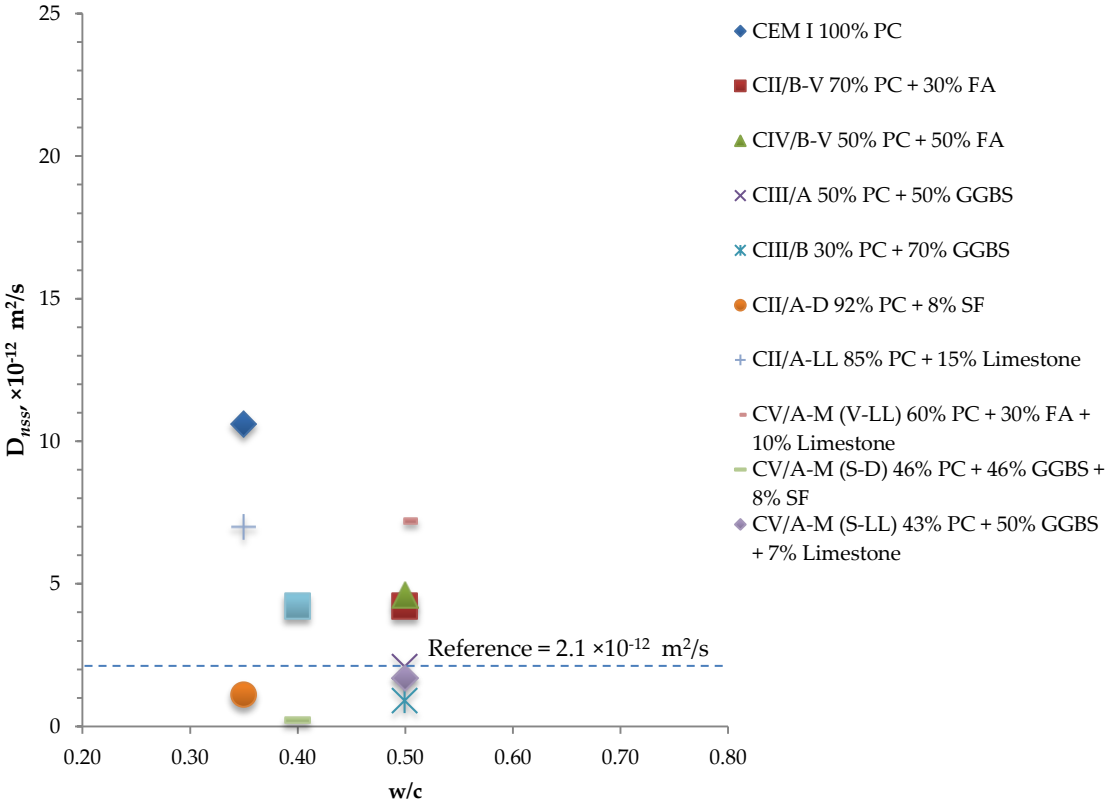


Figure 4.6 **Performance of 50 weeks XS3 class concrete, CEN TS 12390-11:2010**

4.3 EQUIVALENT DURABILITY PERFORMANCE WITH CEN TS 12390-11:2010

Following Table F.1 in BS EN 206-1:2000, maximum water-cement ratio and compressive strength for XS3 and XD3 exposure environment is fixed at 0.45 and 45 N/mm^2 with minimum cement content of 340 kg/m^3 and 320 kg/m^3 for XS3 and XD3 respectively for the intended working life of 50 years. For the purpose of this thesis, the diffusion coefficient performance of the normalised concrete mix is plotted against water-cement ratio for the equivalent compressive strength. Another important factor identified in the literature was water-cement ratio and this is plotted against compressive strength.

Equivalent durability is normalised and compared at 40 N/mm^2, 50 N/mm^2 and 0.45 water-cement ratio and this can be referred to in APPENDIX D. Although the compressive strengths normalisation deviated from BS EN 206-1:2000 recommendations, it allows interpolation to the recommended compressive strength relatively easily when needed.

Minimum cement content is not normalised for equivalent durability as the range of concrete mixes tested are not adequate for comparison. Furthermore, literature review shows that water-cement ratio and the cement content are often interdependent (in many sets of experimental data, the w/c ratio was lowered by increasing the cement content) and their effects with respect to chloride resistance are limited at water-cement ratio tested within the scope of this thesis.

Intrinsic to BS EN 206-1:2000 is the view that the driver for durability in chloride exposure environment is the water-cement ratio and the minimum cement content. On this standpoint, strength is viewed mainly as the mechanical property for structural integrity and does not have a significant role in durability. However, this is continually being challenged by some researchers. The normalisation procedure involving two strength comparisons may shed some light on this subject.

4.3.1 Equivalent performance at 20 weeks

Normalised values are based on the 28 days compressive strength test and 20 weeks test results. Figure 4.7 to Figure 4.9 and Table 4.3 show the normalised D_{nss} for 40 N/mm^2, 50 N/mm^2 and 0.45 water-cement ratio.

4.3.1.1 Normalised equal strength of 40 N/mm^2

Performance of CEM I and CII/A-LL cement is not featured in the normalised data because at their respective water-cement ratio, the D_{nss} values attained are well above 25 × 10^{-12} m^2/s. To put this into perspective, the optimum design specification performance for a new crossing proposal in

Scotland is 5.5×10^{-12} m²/s. As seen in Figure 4.7, the reference mix, CIII/A described in Section 4.1.2 performs better than all other mixes at this strength.

4.3.1.2 Normalised equal strength of 50 N/mm²

The best performance at an equal strength of 50 N/mm² are the blastfurnace cements as shown in Figure 4.8. The CIII/A mix with 50% ggbs performs better than the 70% ggbs mix (CIII/B) (1.2×10^{12} m²/s vs. 1.2×10^{-12} m²/s) and at a higher water-cement ratio (0.41 vs. 0.37). CEM I is still absent from the figure although CII/A-LL is shown to attain 18×10^{-12} m²/s.

4.3.1.3 Normalised equal water-cement ratio of 0.45

At an equal water-cement ratio of 0.45, it can be seen in Figure 4.9 that the strength of the mixes ranges from 22 N/mm² for CIV/B-V to 53.5 N/mm² for CII/A-D. Despite the higher compressive strength of the silica fume mix, CIII/A and CIII/B mixes gives on average double the performance at a lower – 37.5 N/mm² and 33 N/mm² – strength.

4.3.2 Equivalent performance at 50 weeks

Normalised values are based on the 28 days compressive strength test and 50 weeks test results. Figure 4.10 to Figure 4.12 and Table 4.3 give the normalised 50 weeks D_{nss} value for 40 N/mm², 50 N/mm² and 0.45 water-cement ratio.

4.3.2.1 Normalised equal strength of 40 N/mm²

At 50 weeks age, normalised D_{nss} values are less varied compared to the 20 weeks results. Figure 4.10 shows, apart from CEM I that is still absent and the high D_{nss} value of 17.4×10^{-12} m²/s for CII/A-LL mix, other mixes are below 5×10^{-12} m²/s. Nevertheless, ggbs mixes, both CIII/A and CIII/B that has a low 20 weeks D_{nss} remains the best performing. However, fly ash mix is improving very rapidly compared to its earlier 20 weeks value of 7.2×10^{-12} m²/s to 3.6×10^{-12} m²/s for the reference, whilst CIV/B-V reduces from 8.2×10^{-12} m²/s to 4.2×10^{-12} m²/s.

4.3.2.2 Normalised equal strength of 50 N/mm²

The similar trend continues with 50 N/mm² equal strength shown in Figure 4.11. CII/A-D mix is at this strength is now better than the fly ash mixes at 2.8×10^{-12} m²/s vs. 3.8×10^{-12} m²/s (CII/B-V) and 4.2×10^{-12} m²/s (CIV/B-V) with higher water-cement ratio.

4.3.2.3 Normalised equal water-cement ratio of 0.45

Figure 4.12 shows the performance of concrete, relative to its compressive strength at 0.45 water-cement ratio. Compared to the 20 weeks D_{nss} values, performance of concrete is much closer suggesting overall improvement for all mixes except ggbs that had relatively remained constantly the best at less than 2×10^{-12} m²/s.

4.3.3 Observations

Pre-normalisation, of the 19 concrete mixes cast for the thesis, the 0.4 water-cement ratio ternary blend of CEM I, blastfurnace slag and silica fume (46% + 46% + 8%) or CV/A-M (S-D) gives the best performance for CEN 12390-11 test method. This may be attributed to the compounded benefit of pozzolanic properties of ggbs in binding chlorides thus preventing ingress and the ultra-fine silica fume contributing to particle packing and shutting down interconnected pore spaces. Incidentally it has high compressive strength among the mixes at 28 days (51.5 N/mm²) and the highest compressive strength at 1 year (74.5 N/mm²). CEM I and CII/A-LL concrete are the worst performing with respect to chloride resistance despite the high strength of CEM I at 28 days (53.5 N/mm²) and 1 year (60.5 N/mm²).

Initially, fly ash mixes have high D_{nss} values, averaging 16.3×10^{-12} m²/s and 13.3×10^{-12} m²/s for XD3 and XS3 exposure class respectively. This is probably due to the low compressive strength attained at their early age of around 9 – 13 weeks. However, as strength developed over time, fly ash mixes gain the highest improvement compared to other mixes. This is evident by looking at the age exponential data compared to other mixes tested with NT Build 492 and Multi-regime.

Lower than 5×10^{-12} m²/s, diffusion coefficients do not change significantly over time compared to the values at the higher ranges. This could be attributed either to the ability of concrete to improve further at low D_{nss} value or it has to do with the sensitivity of the test method.

If comparison is made based on EN 206-1 alone, comparatively at 0.45 water-cement ratio, CIII/A mix would only yield about 25% less in strength than that of CEM I at 47 N/mm² whilst, CII/A-D mix would yield 15% more strength at 28 days. The difference in strength at the stated water-cement ratio yields a difference of 22% in favour of the CIII/A on the D_{nss} value tested by the 20 weeks CEN TS 12390-11:2010 method. However, comparing both mixes at an equal strength of 50 N/mm² shows that actually the difference in D_{nss} value is 133% in favour of the CIII/A mix.

This suggests that on a like-for-like comparison, strength plays an important part in determining concrete performance apart from water-cement ratio.

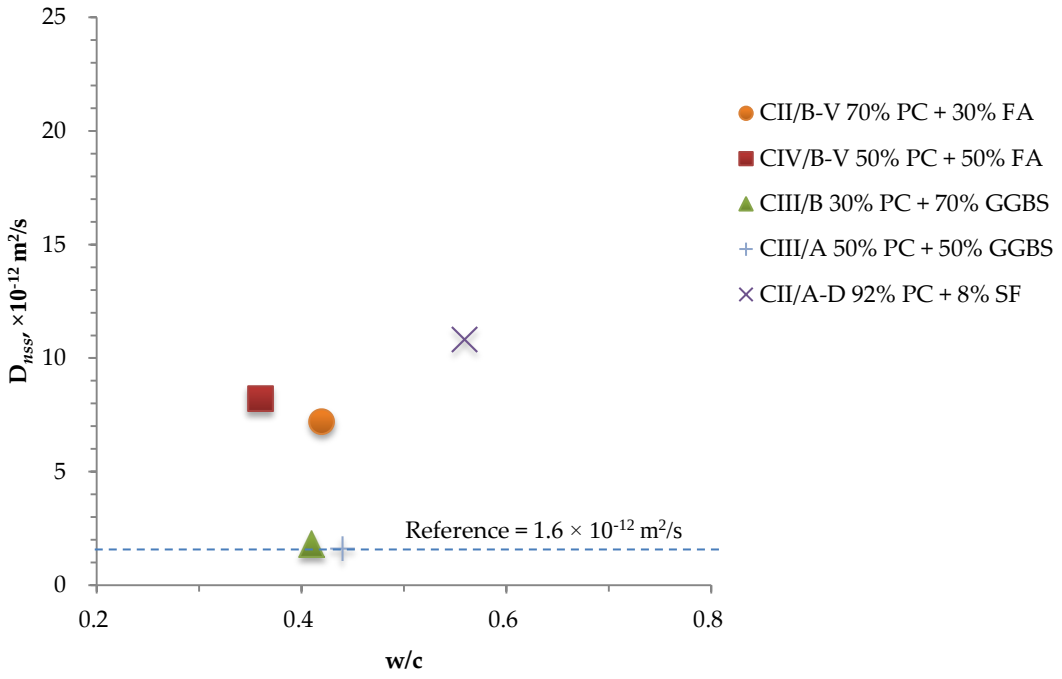


Figure 4.7 **Equivalent performance of concrete, 40 N/mm², 20 weeks, CEN TS 12390-11:2010**

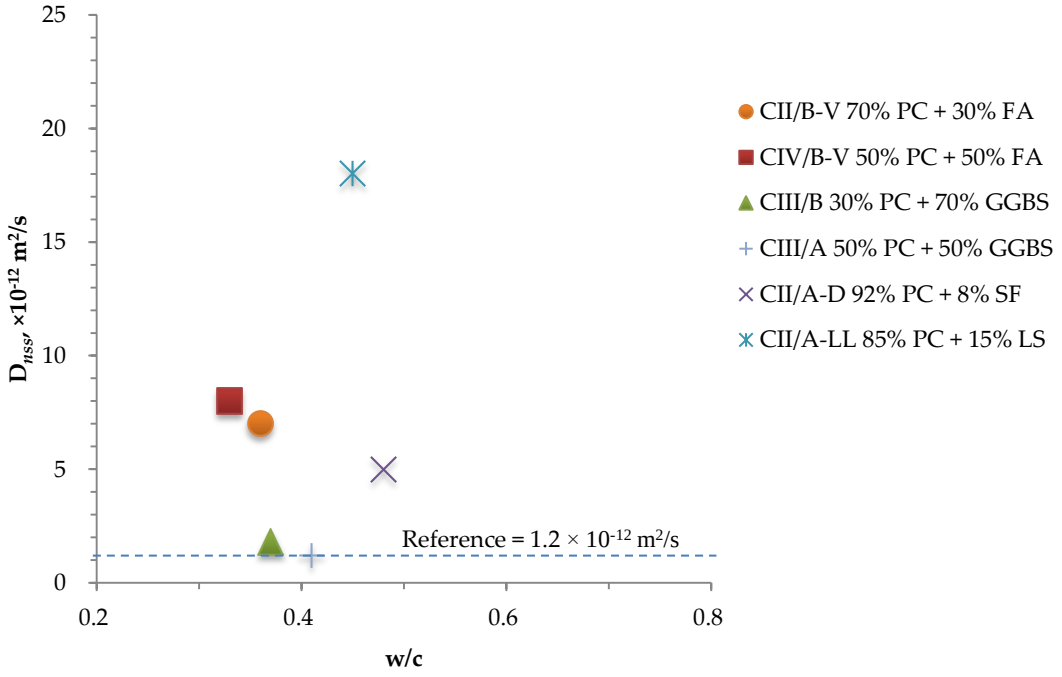


Figure 4.8 **Equivalent performance of concrete, 50 N/mm², 20 weeks, CEN TS 12390-11:2010**

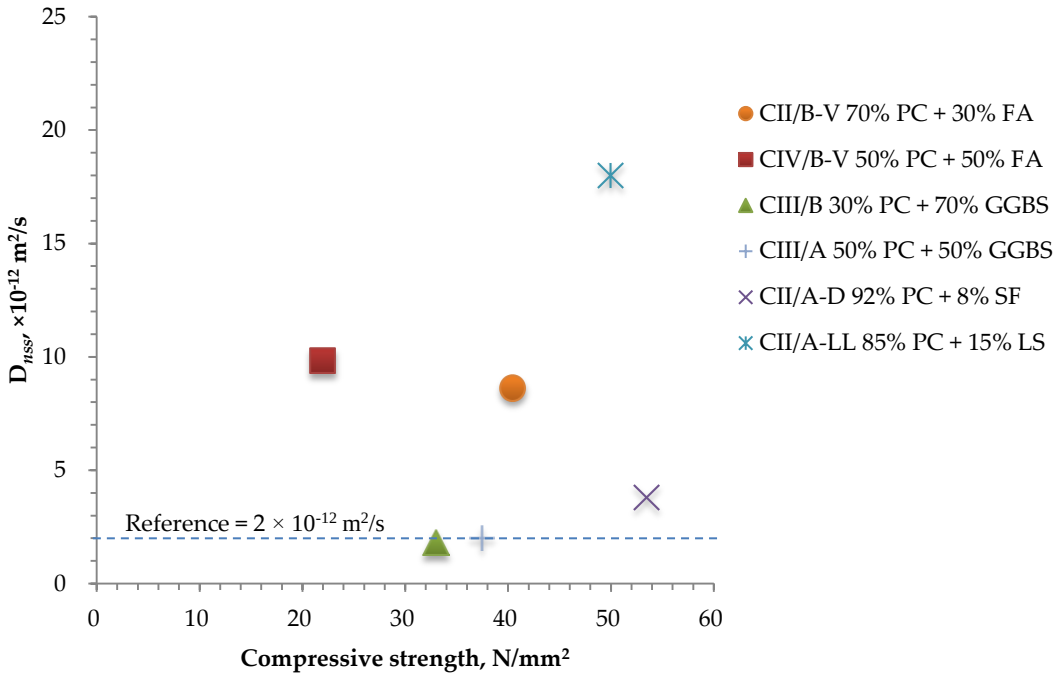


Figure 4.9 **Equivalent performance of concrete, 0.45 w/c, 20 weeks, CEN TS 12390-11:2010**

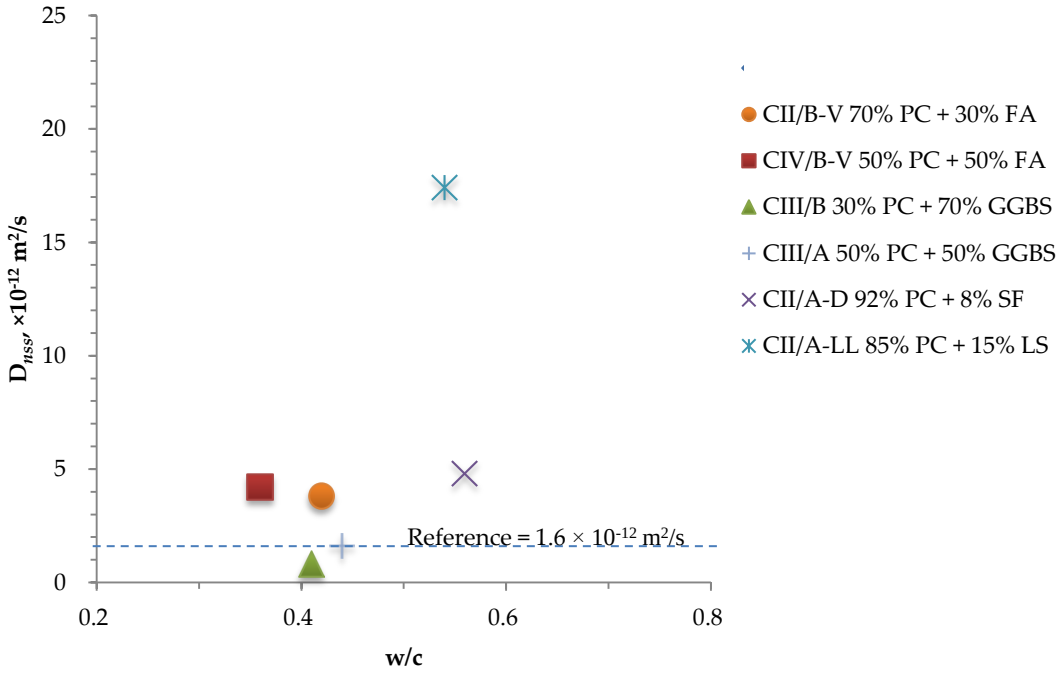


Figure 4.10 **Equivalent performance of concrete, 40 N/mm², 50 weeks, CEN TS 12390-11:2010**

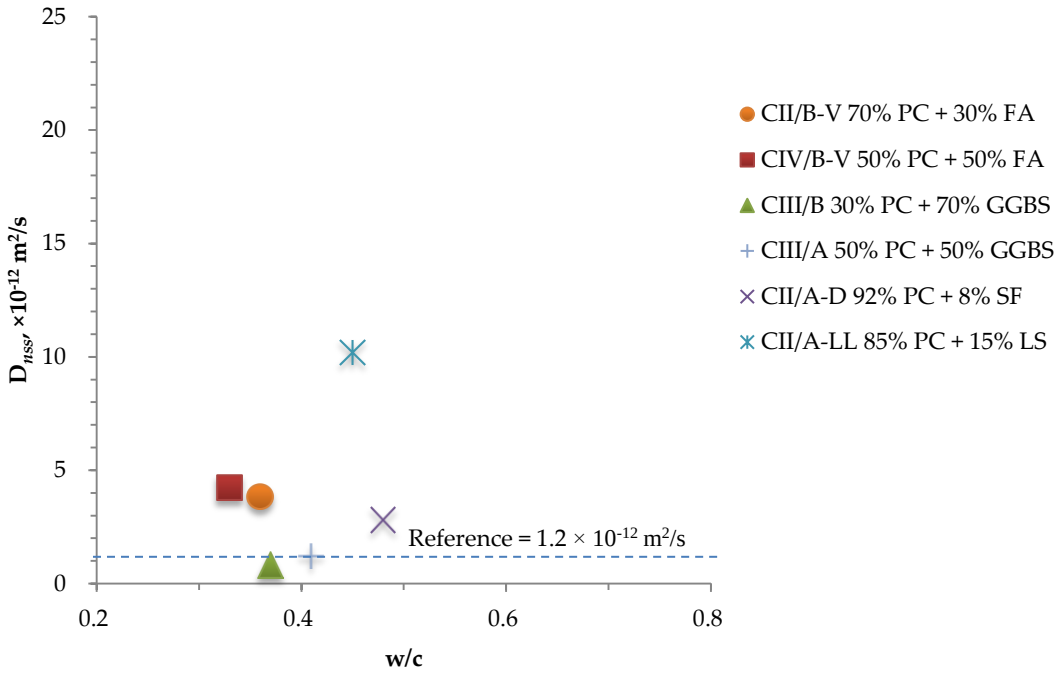


Figure 4.11 **Equivalent performance of concrete, 50 N/mm², 50 weeks, CEN TS 12390-11:2010**

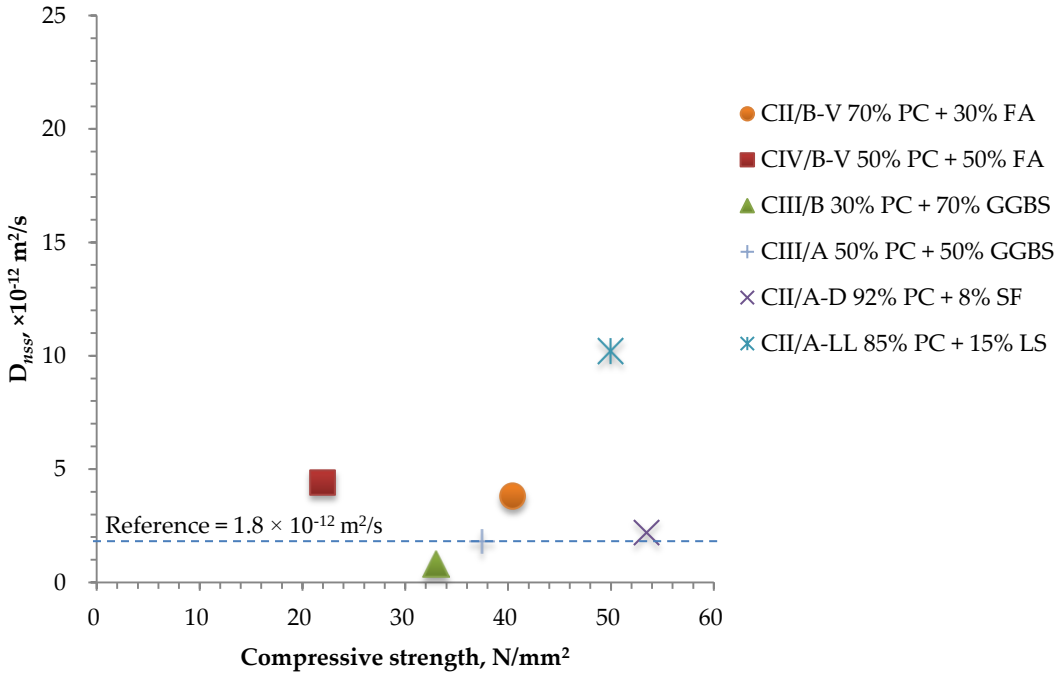


Figure 4.12 **Equivalent performance of concrete, 0.45 w/c, 50 weeks, CEN TS 12390-11:2010**

Table 4.3 Normalised non-steady state D_{nss} values of the test concrete mixes against the benchmark using the CEN TS 12390-11:2010 exposure method

Normalised mixes		20 weeks D_{nss}, × 10^{-12} m²/s		
Mix code	EN 197 notation	40 N/mm²	50 N/mm²	0.45 w/c
N1	CEM I	-[A]	-	-
N2	CII/B-V	7.2	7	8.6
N3	CIV/B-V	8.2	8	9.8
N4	CIII/A	1.6	1.2	2
N5	CIII/B	1.8	1.8	1.8
N6	CII/A-D	10.8	5	3.8
N7	CII/A-LL	-	18	18

Normalised mixes		50 weeks D_{nss}, × 10^{-12} m²/s		
Mix code	EN 197 notation	40 N/mm²	50 N/mm²	0.45 w/c
N1	CEM I	-	-	-
N2	CII/B-V	3.8	3.8	3.8
N3	CIV/B-V	4.2	4.2	4.4
N4	CIII/A	1.6	1.2	1.8
N5	CIII/B	0.8	0.8	0.8
N6	CII/A-D	4.8	2.8	2.2
N7	CII/A-LL	17.4	10.2	10.2

Note:
Reference mix = N4; indicated in the box
[A] denotes D_{nss} value of >25× 10^{-12} m²/s

CHAPTER 5. DIFFUSION COEFFICIENT BENCHMARK USING THE NT BUILD 492 TEST METHOD

5.1 INTRODUCTION

Similar to the earlier section, the test measures the baseline apparent non steady-state migration (D_{nssm}) values for concrete specified under BS 8500-1:2006 with a rapid non steady-state test. The goal is to gauge whether both CEN TS 12390-11:2010 and NT Build 492 tests can give similar values or at the least give similar rank order of resistance with respect to chloride resistance at equal strength and water-cement ratio.

5.1.1 Performance at all ages

Figure 5.1 to Figure 5.6 give the apparent D_{nssm} values for all concrete at their respective time of testing. Data presented are the average values from 2 test cylinders. From this, 4 measurements of average chloride depths were taken and the diffusion coefficient is calculated. Outliers are determined visually by observation of the overall data especially regression trends and the expected behaviour. These outliers were excluded from the calculation of the average value presentation. Raw data showing each measured data points is included in APPENDIX F.

Figure 5.1 and Figure 5.2 show the evolution of chloride diffusion coefficient as measured by NT Build 492 test method. It can be seen that the trend is similar to the results of CEN TS 12390-11:2010, where below 5×10^{-12} m^2/s the diffusion coefficient values does not change significantly with age. Above 5×10^{-12} m^2/s, the reduction of coefficient diffusion values can be seen as significant for several cements. These raw results also show that fly ash cements generally show the highest rate of improvement for diffusion resistance than other cements.

5.1.2 Performance at 20 weeks

Figure 5.3 and Figure 5.4 shows the interpolated performance of mixes at 20 weeks equal age for XD3 and XS3 exposures respectively.

5.1.3 Performance at 50 weeks

Figure 5.5 and Figure 5.6 shows the interpolated performance of mixes at 50 weeks equal age for XD3 and XS3 exposures respectively.

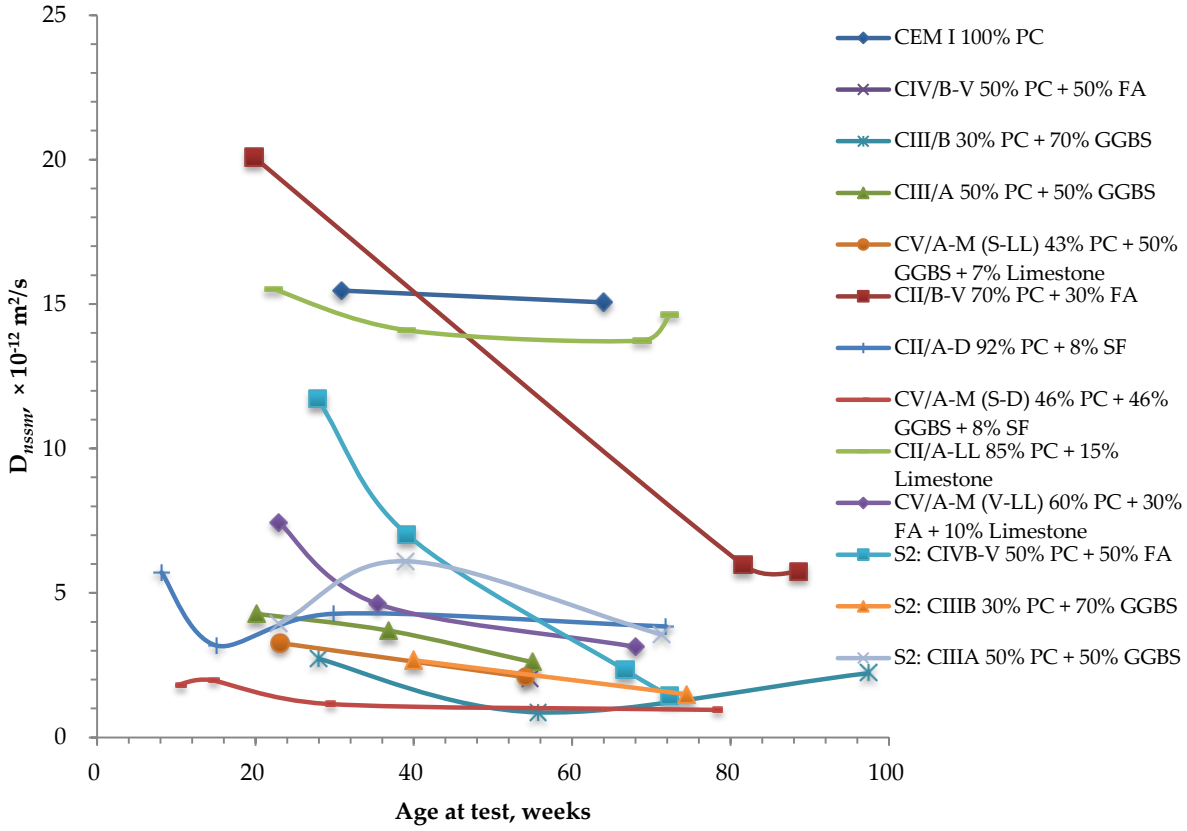


Figure 5.1 **Measured NT Build 492 D_{nssm} values for XD class concretes**

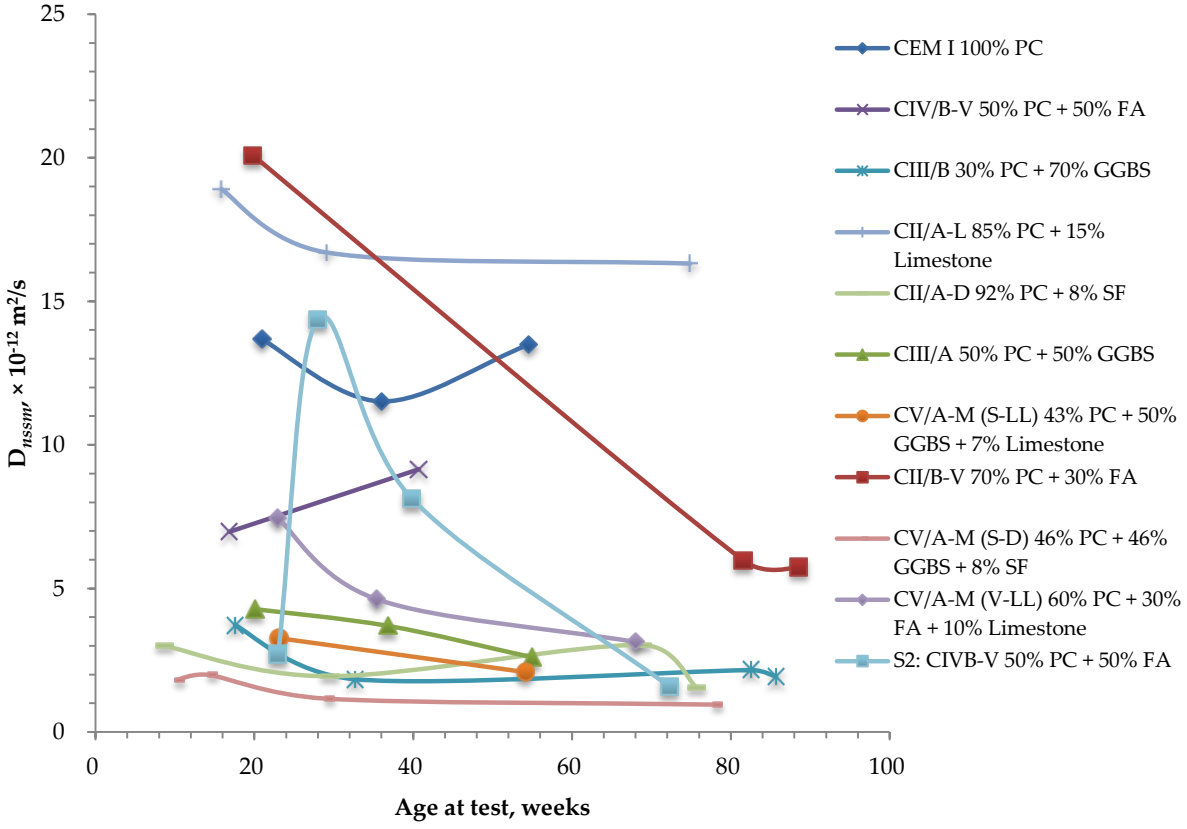


Figure 5.2 **Measured NT Build 492 D_{nssm} values for XS class concretes**

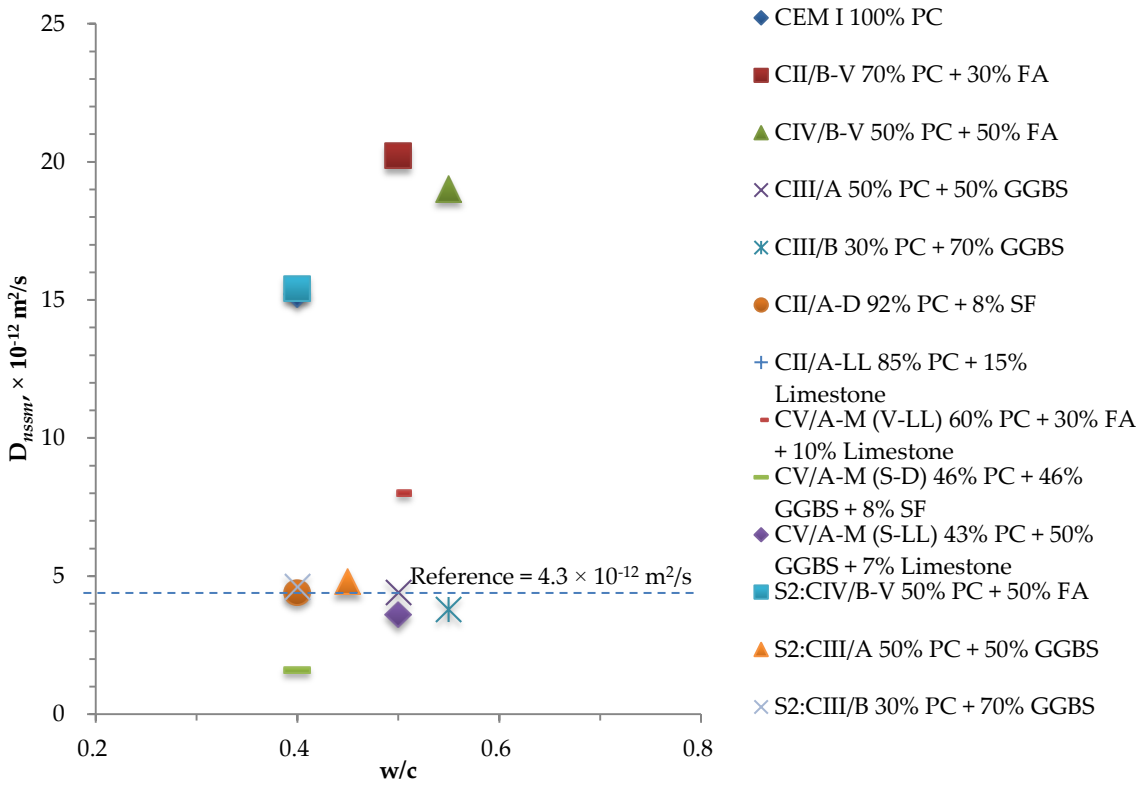


Figure 5.3 **Performance of 20 weeks XD3 class concrete, NT Build 492**

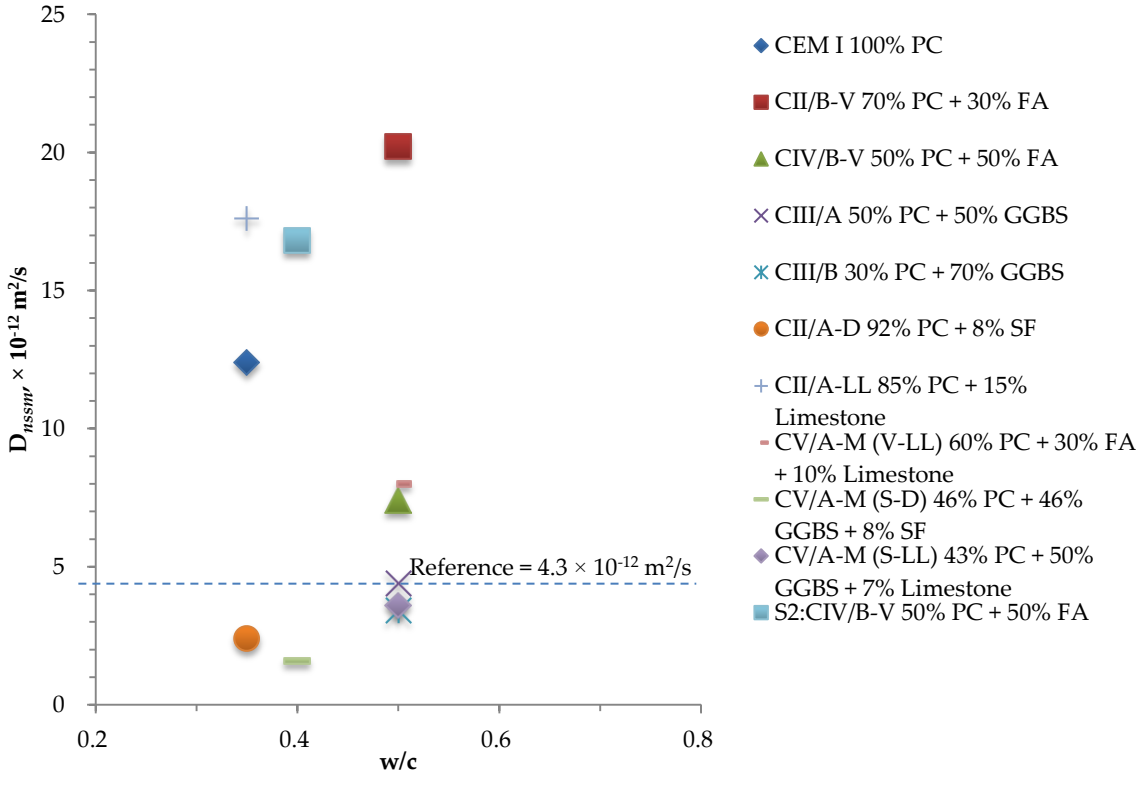


Figure 5.4 **Performance of 20 weeks XS3 class concrete, NT Build 492**

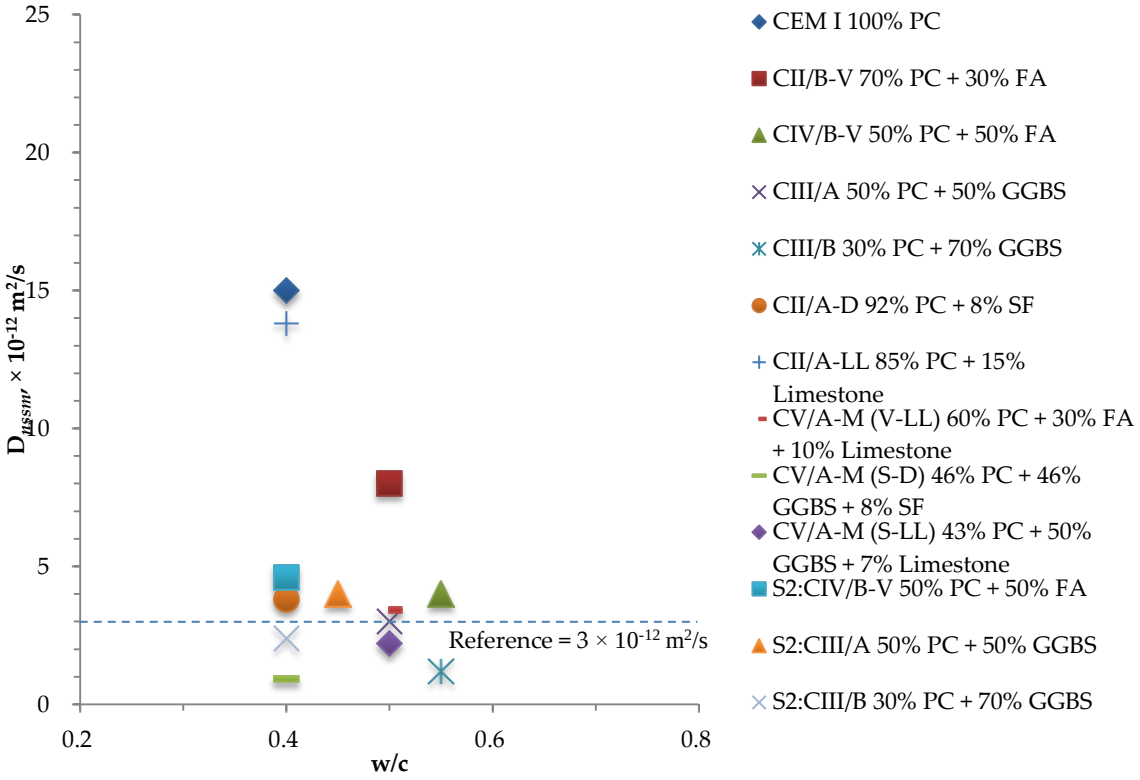


Figure 5.5 Performance of 50 weeks XD3 class concrete, NT Build 492

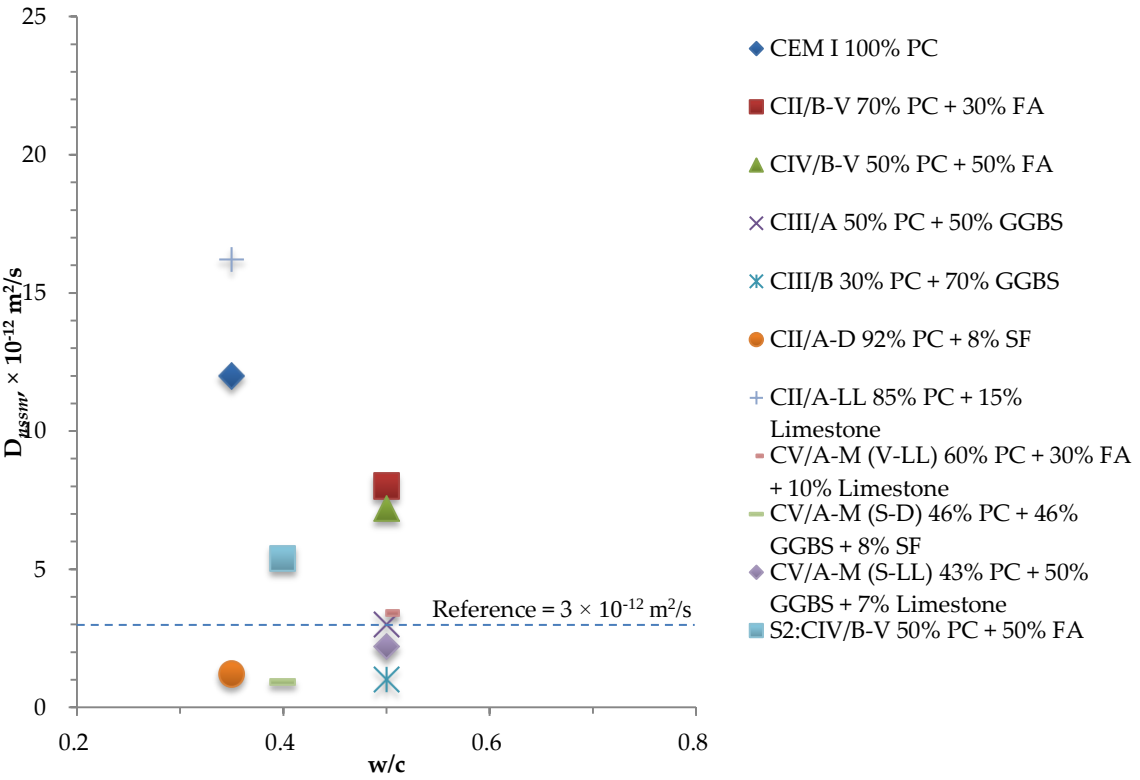


Figure 5.6 Performance of 50 weeks XS3 class concrete, NT Build 492

5.2 EQUIVALENT DURABILITY PERFORMANCE WITH NT BUILD 492

The next step is to determine the equivalent durability performance of NT Build 492 against the specific performance at 40 N/mm^2, 50 N/mm^2 and 0.45 water-cement ratio similar to the previous chapter, to enable comparison in Chapter 7.

5.2.1 Equivalent performance at 20 weeks

Equivalent performance values are based on the 28 days compressive strength test and 20 weeks normalisation. These are shown in Figure 5.7 to Figure 5.9 and Table 5.1.

5.2.1.1 Normalised equal strength of 40 N/mm^2

CEM I and CII/A-LL are not featured in the normalisation because their values are significantly higher than the 25 ×10^{-12} m^2/s threshold set out earlier in chapter 4. At this age, the performance of the fly ash mixes are poor as seen in Figure 5.7 with CII/B-V attaining 17.4 × 10^{-12} m^2/s and followed by CIV/B-V at 15.2 × 10^{-12} m^2/s. By comparison, the ggbs mixes attained 3.8 × 10^{-12} m^2/s and 3.2 × 10^{12} m^2/s (CIII/A and CIII/B) respectively.

5.2.1.2 Normalised equal strength of 50 N/mm^2

All concretes are featured in Figure 5.8, the ranking of normalised concrete mixes from best to worst is CIII/B> CIII/A> CII/A-D> CIV/B-V> CII/BV> CEM I and CII/A-LL ranging from 19.8 × 10^{12} m^2/s to 3.2 × 10^{-12} m^2/s.

5.2.1.3 Normalised equal water-cement ratio of 0.45

It can be seen in Figure 5.9 that there is a change of ranking at the top of the figure where the limestone mix is slightly better, i.e. lower D_{nssm} value than CEM I (20 × 10^{-12} m^2/s vs. 21 × 10^{-12} m^2/s). At the normalised equal water-cement ratio of 0.45, CII/A-LL has a compressive strength of 50 N/mm^2 compared to CEM I at 47 N/mm^2.

5.2.2 Equivalent performance at 50 weeks

Normalised values are based on the 28 days compressive strength test and 50 weeks test results. These are shown in Figure 5.10 to Figure 5.12 Table 5.1.

5.2.2.1 Normalised equal strength of 40 N/mm²

At 50 weeks, concretes expected to perform well in chloride environment started to group closer together. These are in order of best to worse, CIII/A> CIII/B> CIV/B-V> CII/B-V and lastly CII/A-D ranging from 2×10^{-12} m²/s to 13×10^{-12} m²/s. CEM I and CII/A-LL did not appear in Figure 5.10.

5.2.2.2 Normalised equal strength of 50 N/mm²

The ranking of concrete did not change at this strength shown in Figure 5.11. CEM I and CII/A-LL are the worst performing concrete, their values close to 20×10^{-12} m²/s whilst CII/A-D concrete is performing better at this strength compared to 40 N/mm².

5.2.2.3 Normalised equal water-cement ratio of 0.45

Figure 5.12 refers to the normalised D_{nssm} value at the equal water-cement ratio of 0.45. The spread of concrete strength from 22 N/mm² to 53 N/mm² shows the performance of all concrete with regards to their respective compressive strength. It shows that high strength concrete for example CII/A-D does not necessarily have the best performance.

5.2.3 Observations

The overall results show that the diffusion resistance of CEM I and CII/A-LL does not improve with age as well as other concretes. Apart from these two, other concretes with D_{nssm} value above 5×10^{-12} m²/s have improved over time, especially the fly ash mixes. Ggbs concrete still performs the best with the general trend of low initial D_{nssm} values of lower than 5×10^{-12} m²/s and continually but modestly improving with age.

Due to the low initial strength of the fly ash mixes, their performance during early age tests were far from their potential chloride resisting properties. As strength development progresses and pore space becomes refined due to continuous pozzolanic reaction, chloride resistance performance of fly ash concrete improved. However, it could be argued that it is better to start with a lower diffusion coefficient in the first place as demonstrated with ggbs concretes.

Unexpected results can sometimes be observed with this test. Figure 5.2 shows for CIV/B-V mix the D_{nssm} value measured 5 weeks apart shows a big jump from an average of 2.7×10^{-12} m²/s to 14.3×10^{-12} m²/s. Test results and calculations have been checked but nothing could be found to suggest an error. Furthermore, this result could not be regarded as incorrect as data available on another CIV/B-V mix with the same water-cement ratio but different cement content (less 20 kg/m³ than the former) follows the 14.3×10^{-12} m²/s trend over age.

Normalisation of mixes to 40 N/mm^2, 50 N/mm^2 and 0.45 water-cement ratio shows the relative performance of each concrete type in chloride environment more clearly. Similar to CEN TS 12390-11:2010 test method, ggbs mix came out the best, followed by fly ash and silica fume. CEM I and CII/A-LL showed poor performance in this test.

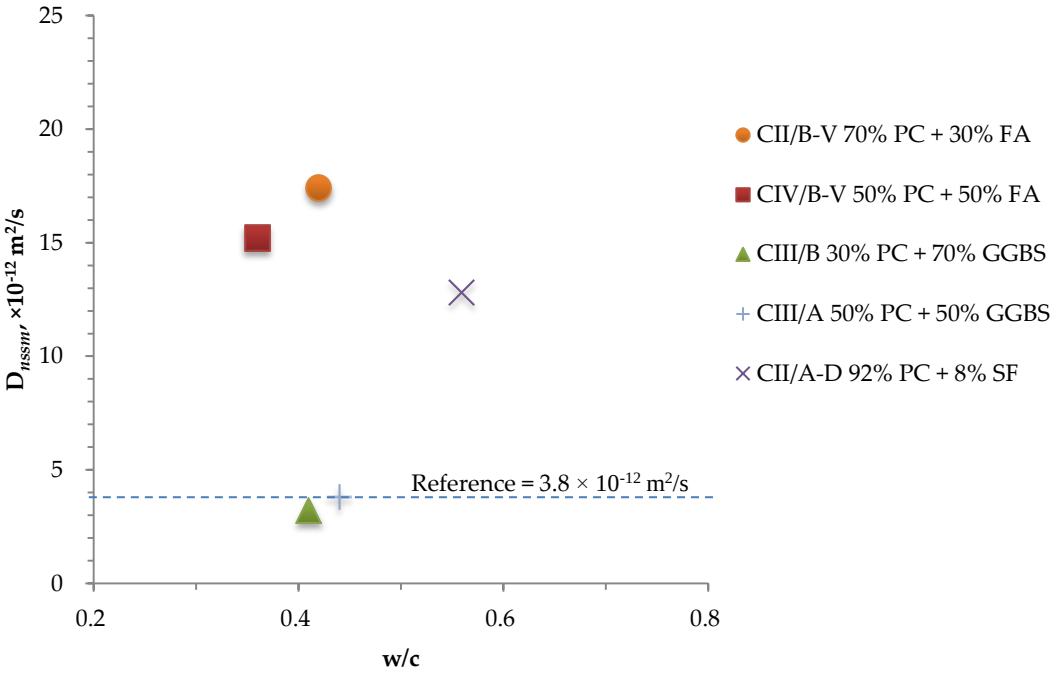


Figure 5.7 **Equivalent performance of concrete, 40 N/mm², 20 weeks, NT Build 492**

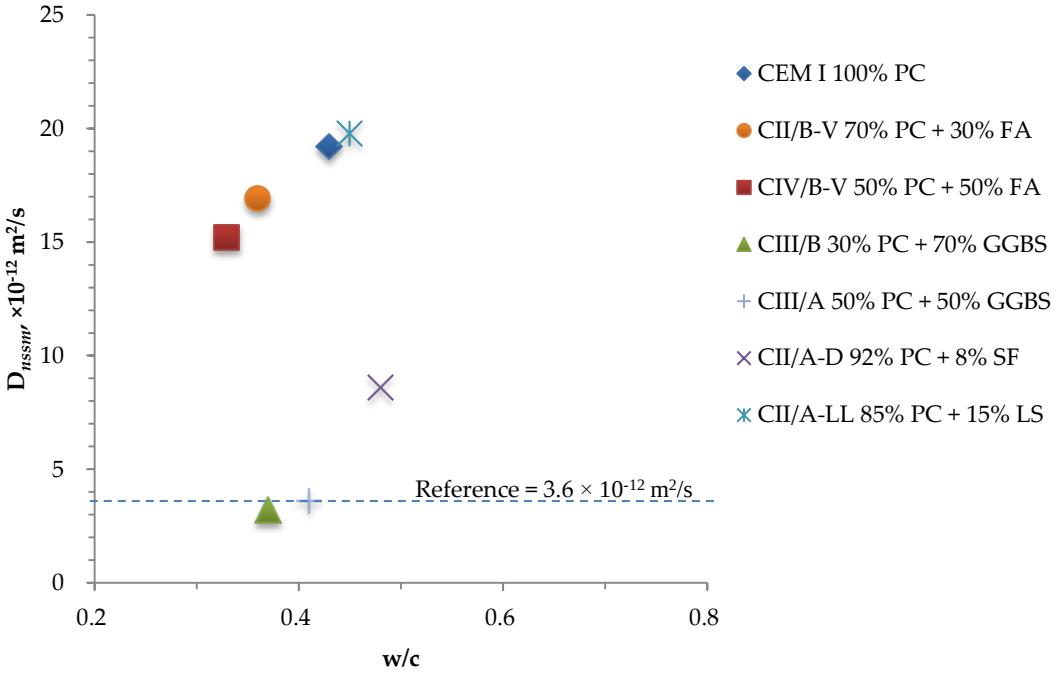


Figure 5.8 **Equivalent performance of concrete, 50 N/mm², 20 weeks, NT Build 492**

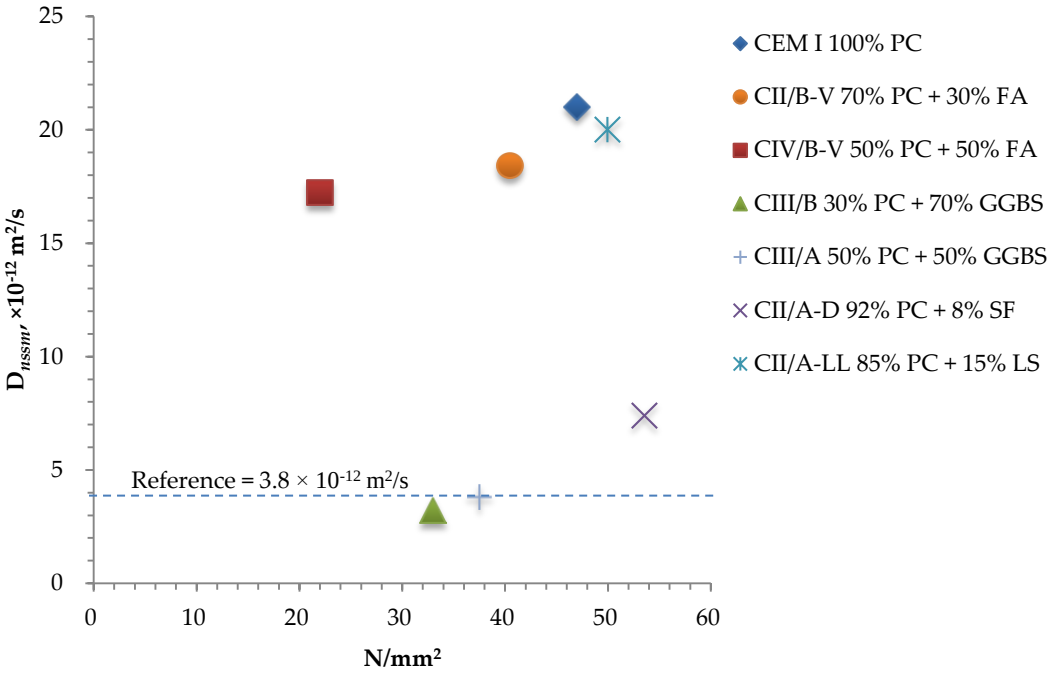


Figure 5.9 **Equivalent performance of concrete, 0.45 w/c, 20 weeks, NT Build 492**

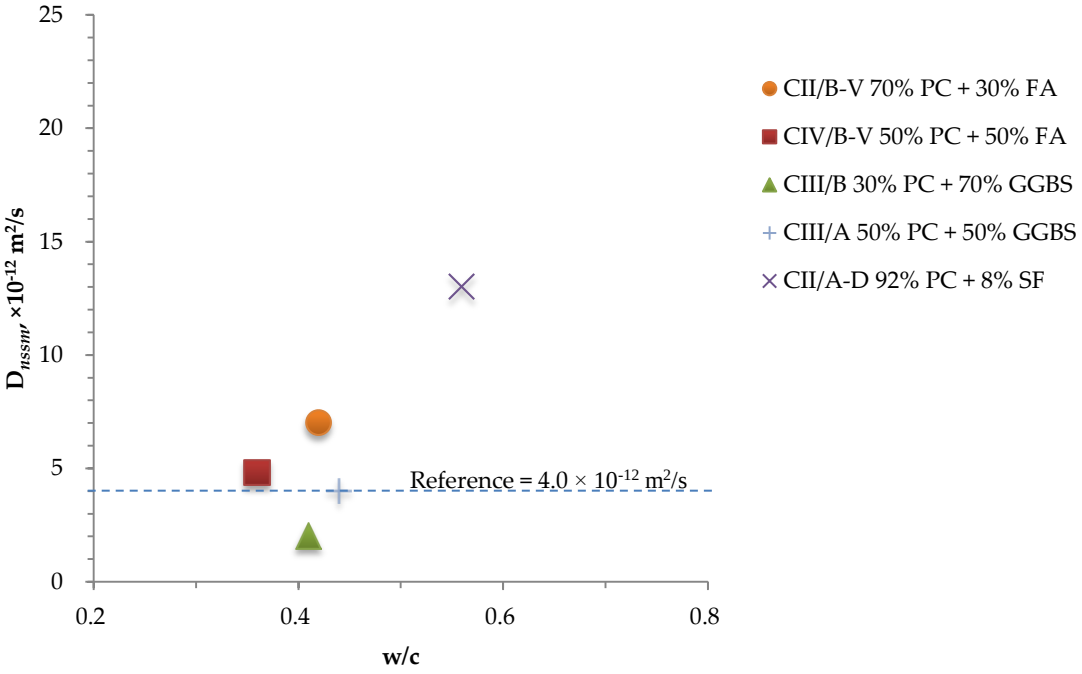


Figure 5.10 **Equivalent performance of concrete, 40 N/mm², 50 weeks, NT Build 492**

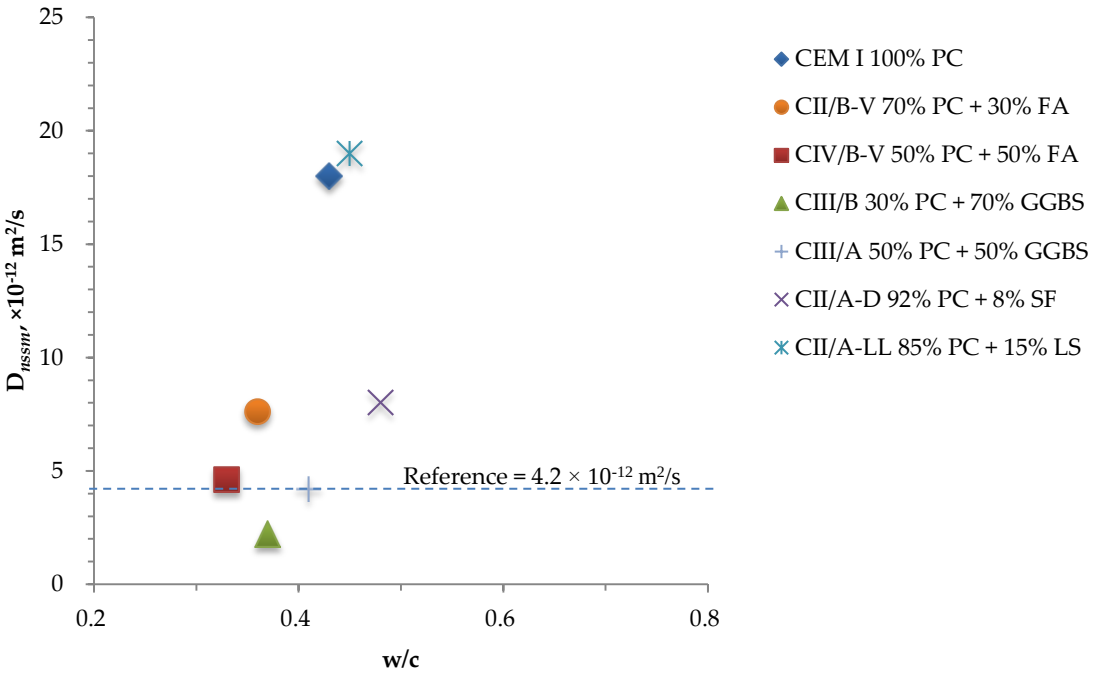


Figure 5.11 **Equivalent performance of concrete, 50 N/mm², 50 weeks, NT Build 492**

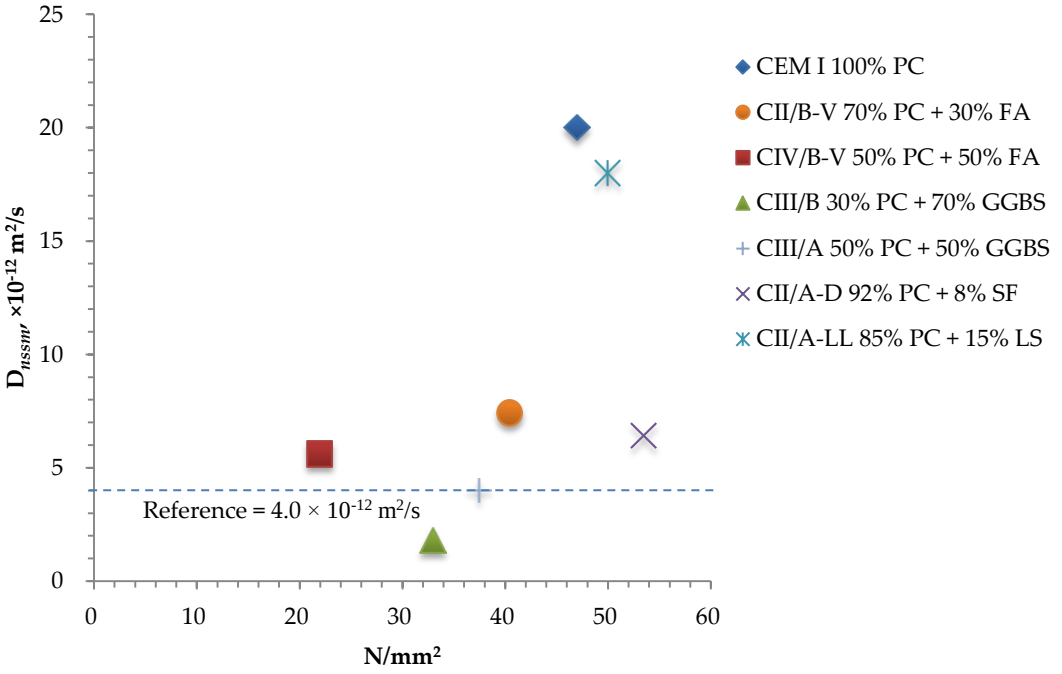


Figure 5.12 **Equivalent performance of concrete, 0.45 w/c, 50 weeks, NT Build 492**

Table 5.1 Normalised non-steady state D_{nssm} values of the test concrete mixes against the benchmark using the NT Build 492 exposure method

Normalised mixes		20 weeks D_{nssm}, $\times 10^{-12}$ m²/s		
Mix code	EN 197 notation	40 N/mm²	50 N/mm²	0.45 w/c
N1	CEM I	-[A]	19.2	21.0
N2	CII/B-V	17.4	16.9	18.4
N3	CIV/B-V	15.2	15.2	17.2
N4	CIII/A	3.8	3.6	3.8
N5	CIII/B	3.2	3.2	3.2
N6	CII/A-D	12.8	8.6	7.4
N7	CII/A-LL	-	19.8	20.0

Normalised mixes		50 weeks D_{nssm}, $\times 10^{-12}$ m²/s		
Mix code	EN 197 notation	40 N/mm²	50 N/mm²	0.45 w/c
N1	CEM I	-	18.0	20.0
N2	CII/B-V	7.0	7.6	7.4
N3	CIV/B-V	4.8	4.6	5.6
N4	CIII/A	4.0	4.2	4.0
N5	CIII/B	2.0	2.2	1.8
N6	CII/A-D	13.0	8.0	6.4
N7	CII/A-LL	-	19.0	18.0

Note:
Reference mix = N4; indicated in the box
[A] denotes D_{nssm} value of > 25 $\times 10^{-12}$ m²/s

CHAPTER 6. DIFFUSION COEFFICIENT BENCHMARK USING THE MULTI-REGIME TEST METHOD (UNE 83987:2009)

6.1 INTRODUCTION

In this section, the concrete at the limit of BS 8500-1:2006 are tested with the Spanish Standard UNE 83987:2009 or regularly called the Multi-regime test method that gives the steady-state value of D (D_{ssm}). The performance is not directly compared with CEN TS 12390-11:2010 as this test only gives the non steady-state D value. However, the author is looking for the similarity of ranking if there is any between these test methods.

6.1.1 Performance at all ages

Figure 6.1 to Figure 6.6 give the D_{ssm} values for all concrete at their respective time of testing. Data presented are the average D_{ssm} values from the maximum of 3 test discs. Outliers are determined visually by observation of the overall data especially regression trends and the expected behaviour. These outliers were excluded from the calculation of the average value presentation.

Figure 6.1 and Figure 6.2 show the Multi-regime test returns a much narrow range of results for all concrete tested compared to that of CEN TS 12390-11:2010 and NT Build 492. Almost all mixes except CEM I and CII/A-LL mixes are below 5×10^{-12} m^2/s. At this range, concrete does not change significantly over time. The best performing concrete is still the ternary blend of CEM I, ggbs and silica fume (46% + 46% + 8%) with the initial D_{ssm} of 1.2×10^{-12} m^2/s at 15 weeks and 1×10^{-12} m^2/s at 82 weeks. This mix took 10 weeks to complete the test and this was one of the longest test periods.

6.1.2 Performance at 20 weeks

Figure 6.3 and Figure 6.4 show the interpolated performance of concrete mixes at 20 weeks equal age for XD3 and XS3 exposure respectively.

6.1.3 Performance at 50 weeks

Figure 6.5 and Figure 6.6 shows the interpolated performance of concrete mixes at 50 weeks equal age for XD3 and XS3 exposure respectively.

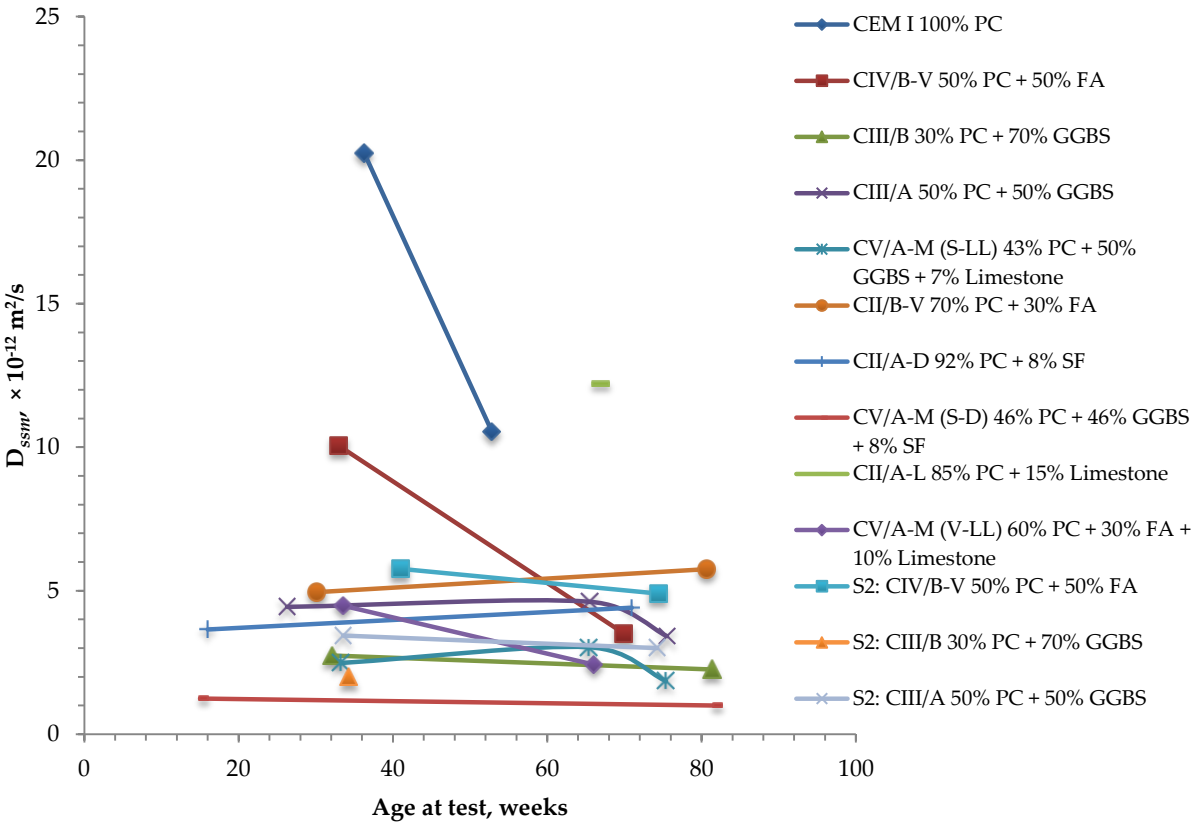


Figure 6.1 **Measured Multi-regime D_{ssm} values for XD3 class concretes**

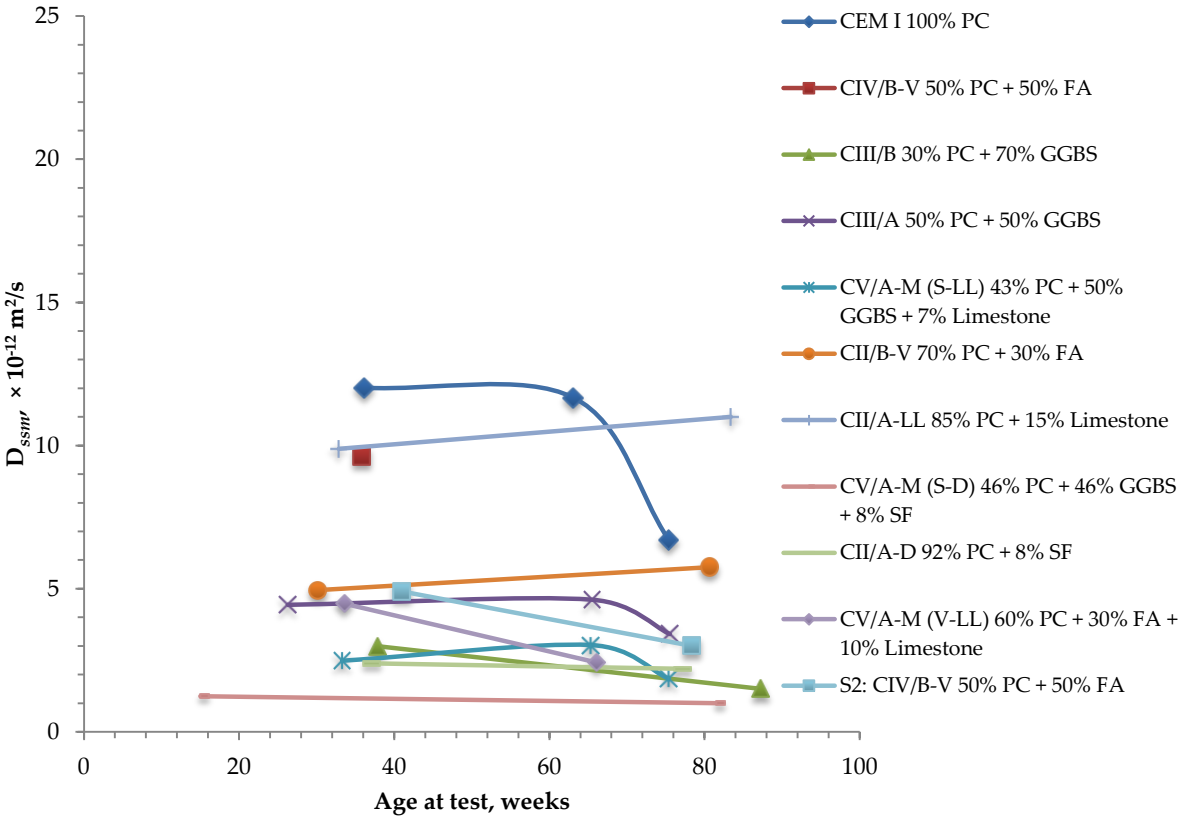


Figure 6.2 **Measured Multi-regime D_{ssm} values for XS3 class concretes**

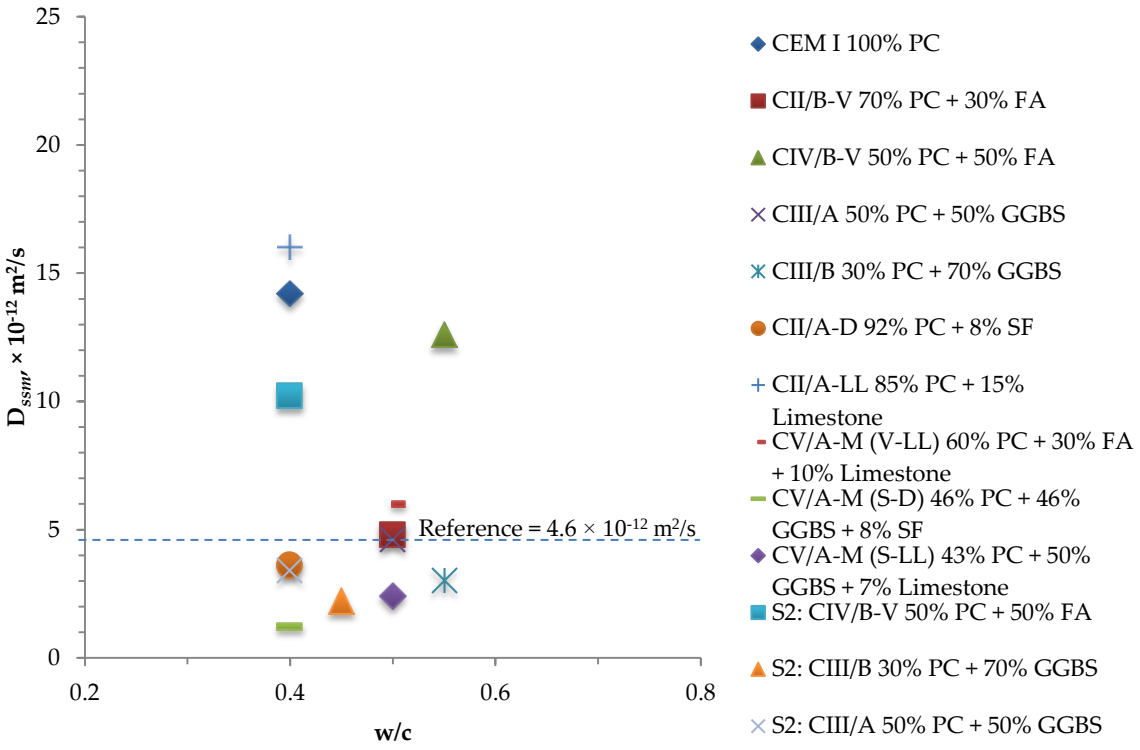


Figure 6.3 Performance of 20 weeks XD3 class concrete, Multi-regime

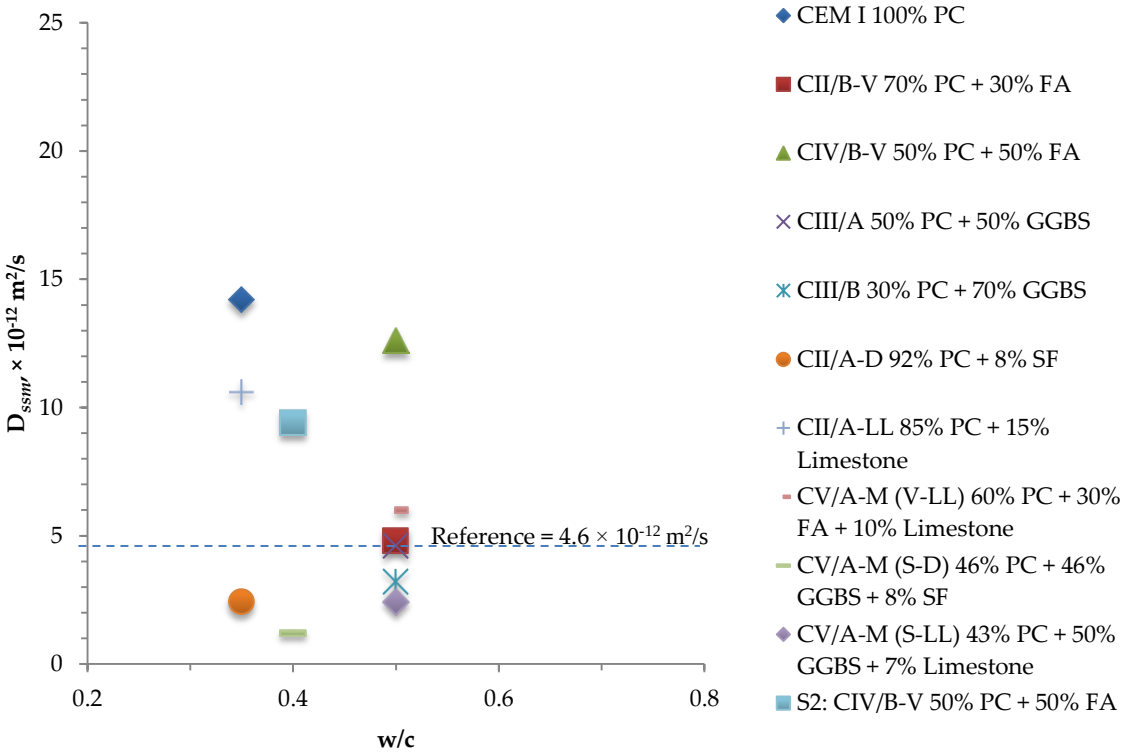


Figure 6.4 Performance of 20 weeks XS3 class concrete, Multi-regime

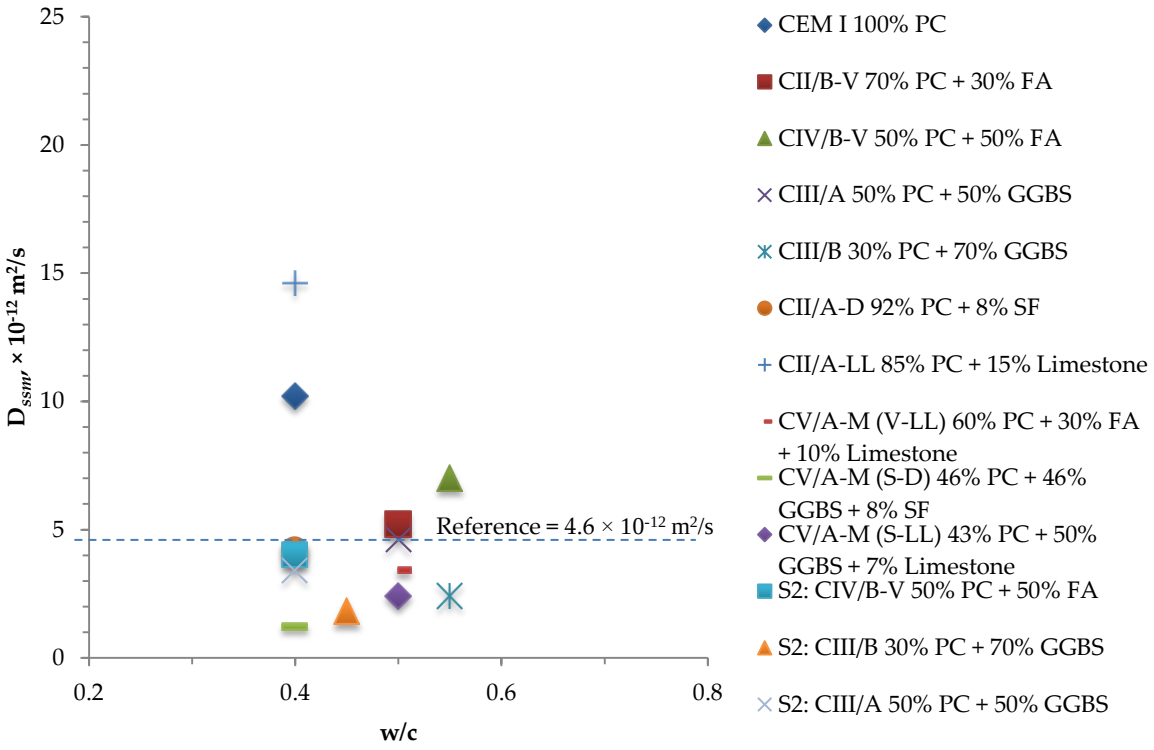


Figure 6.5 Performance of 50 weeks XD3 class concrete, Multi-regime

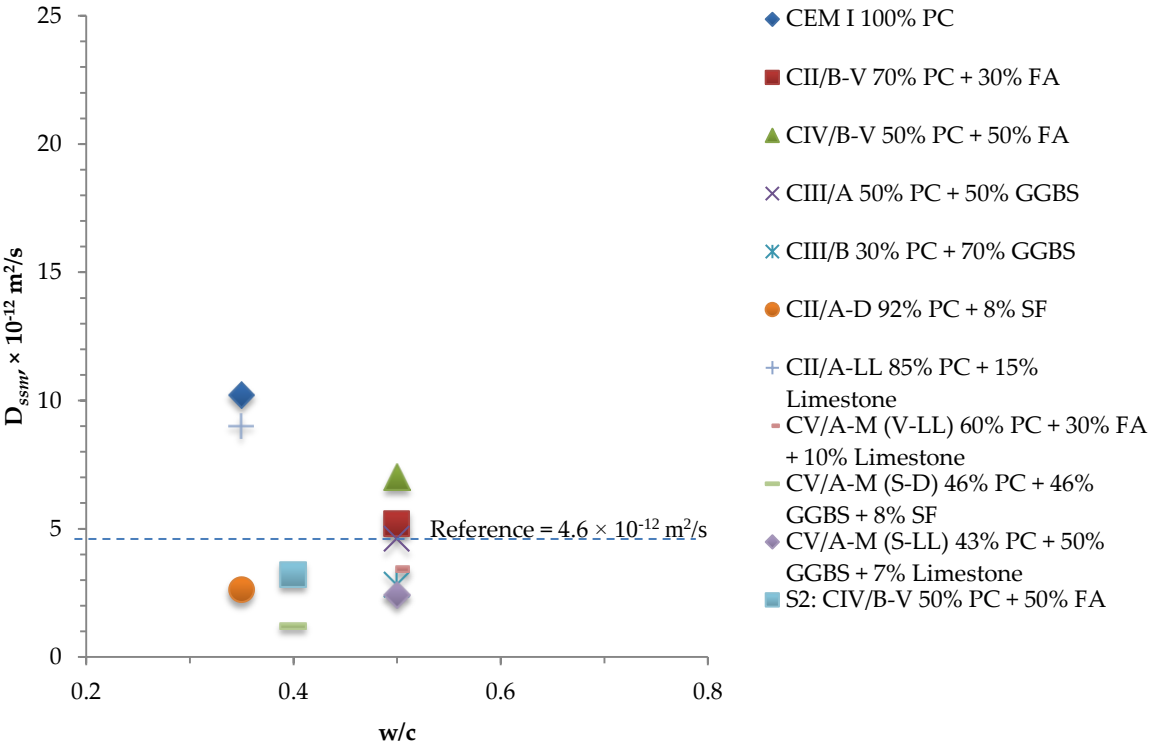


Figure 6.6 Performance of 50 weeks XS3 class concrete, Multi-regime

6.2 EQUIVALENT DURABILITY PERFORMANCE WITH MULTI-REGIME METHOD

Similar to the two preceding chapters, the equivalent durability performance in the multi-regime test is compared at the determined compressive strength of 40 N/mm^2, 50 N/mm^2 and 0.45 water-cement ratio.

6.2.1 Equivalent performance at 20 weeks

Normalised values are based on the 28 days compressive strength test and 20 weeks test results. These are shown in Figure 6.7 to Figure 6.9 and Table 6.1.

6.2.1.1 Normalised equal strength of 40 N/mm^2

The best performing mixes at this age is, in order of best to worst is CIII/B, CII/B-V and CIII/A which is below 5 × 10^{-12} m^2/s. CIV/B-V and CII/A-D mixes follows with D_{ssm} value below 10 ×10^{12} m^2/s. CII/A-LL mix is the worst performing and CEM I has a value of 22 × 10^{-12} m^2/s as shown Figure 6.7.

6.2.1.2 Normalised equal strength of 50 N/mm^2

With the reduction of overall water-cement ratio at 50 N/mm^2 equal strength, performance of all cement is better compared to 40 N/mm^2. However, Figure 6.8 shows that this does not change the ranking.

6.2.1.3 Normalised equal water-cement ratio of 0.45

Figure 6.9 show that the CIII/B mix with the best chloride resistance does not have the highest compressive strength. At 0.45 water-cement ratio, this concrete only yields 33 N/mm^2. This shows that chloride resistance is not solely controlled by strength/ water-cement ratio but binding capacity is equally important. All other mixes apart from CIV/B-V have higher compressive strength than the CIII/B mix at this water-cement ratio (the closest is 37.5 N/mm^2) but their D_{ssm} values are higher by a minimum of 21%.

6.2.2 Equivalent performance at 50 weeks

Normalised values are based on the 28 days compressive strength test and 50 weeks test results. These are shown in Figure 6.10 to Figure 6.12 and Table 6.1

6.2.2.1 Normalised equal strength of 40 N/mm²

At the later age of 50 weeks, the better improvement of fly ash mixes over time can be seen from the CIV/B-V mix. Its 20 weeks D_{ssm} value of 7.4 × 10^{-12} m²/s has reduced to 2.6 ×10^{-12} m²/s which is a reduction of 65%, the highest between all mixes.

6.2.2.2 Normalised equal strength of 50 N/mm²

The reduction of 65% from 20 weeks to 50 weeks is continued for CIV/B-V at the equal strength of 50 N/mm². Figure 6.11 shows that mixes expected to perform well in chloride environment i.e. fly ash and ggbs are hovering at 2 ×10^{-12} m²/s.

6.2.2.3 Normalised equal water-cement ratio of 0.45

Except for the 54% improvement of CIV/B-V mix, other mixes did not change significantly compared to 20 weeks.

6.2.3 Observations

Compared to the two earlier test methods, a steady-state test is designed to give the ultimate durability potential for any particular candidate concrete in the chloride environment. In steady-state flow, chloride binding is no longer an issue as it is considered to be complete and chloride migration in this case un-hindered by binding. The result shows that concretes that are expected to perform well in chloride environment does perform well with the test method.

Between the early age of up to 1 year, continual improvement can be seen especially for the fly ash mixes. Ggbs mixes performs the best with good performance throughout the entire test duration. As with the two earlier test methods, CEM I and CII/A-LL mixes are shown to be inadequate in resisting chloride ion ingress even at a relatively high strength/ low water-cement ratio.

Despite the improvement of concrete over the duration of the test period, the range of result with the multi-regime test is narrower by comparison to the non steady-state tests. This may give credence to the argument that the non-steady tests does lead to a conservative estimate of durability due to the higher D value they return.

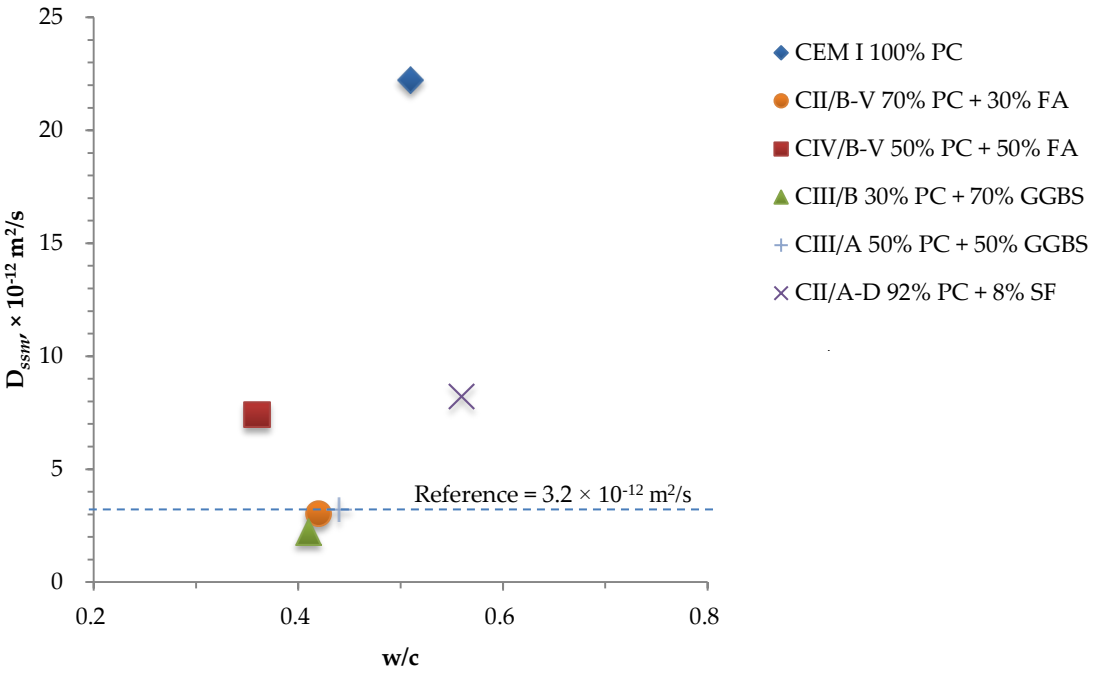


Figure 6.7 **Equivalent performance of concrete, 40 N/mm², 20 weeks, Multi-regime**

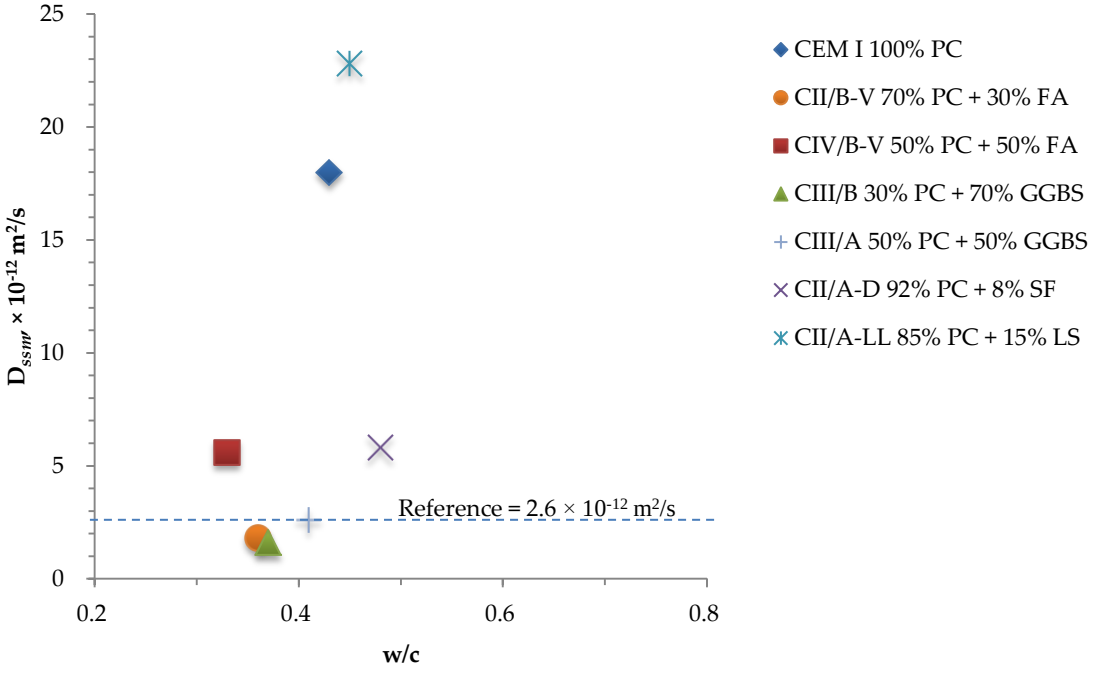


Figure 6.8 **Equivalent performance of concrete, 50 N/mm², 20 weeks, Multi-regime**

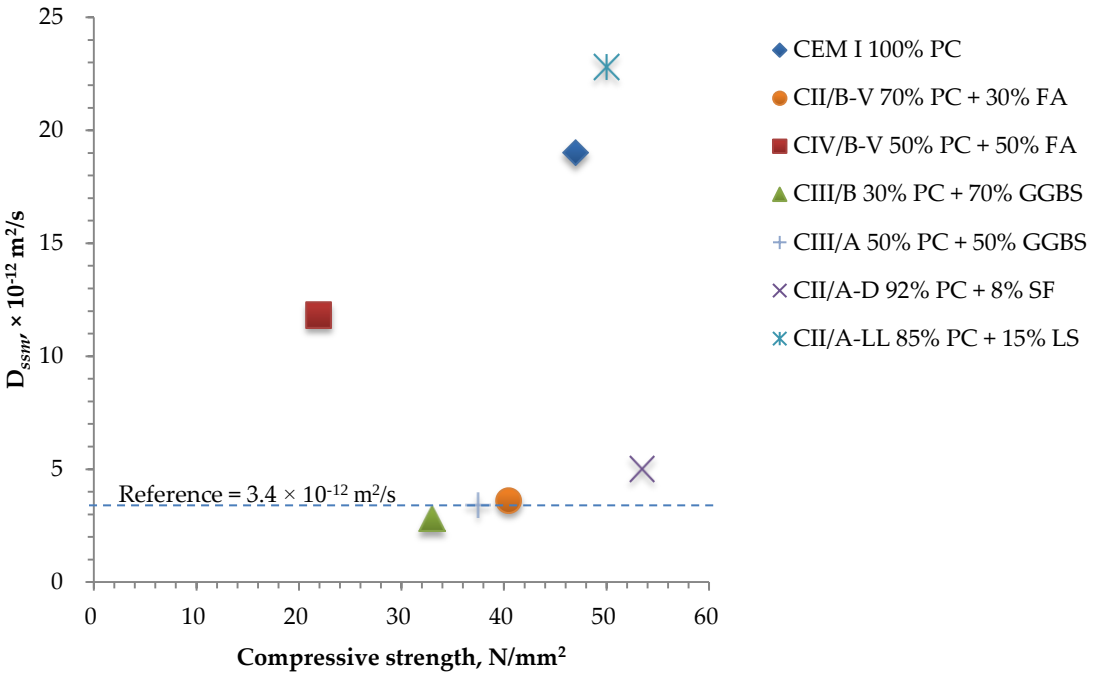


Figure 6.9 **Equivalent performance of concrete, 0.45 w/c, 20 weeks, Multi-regime**

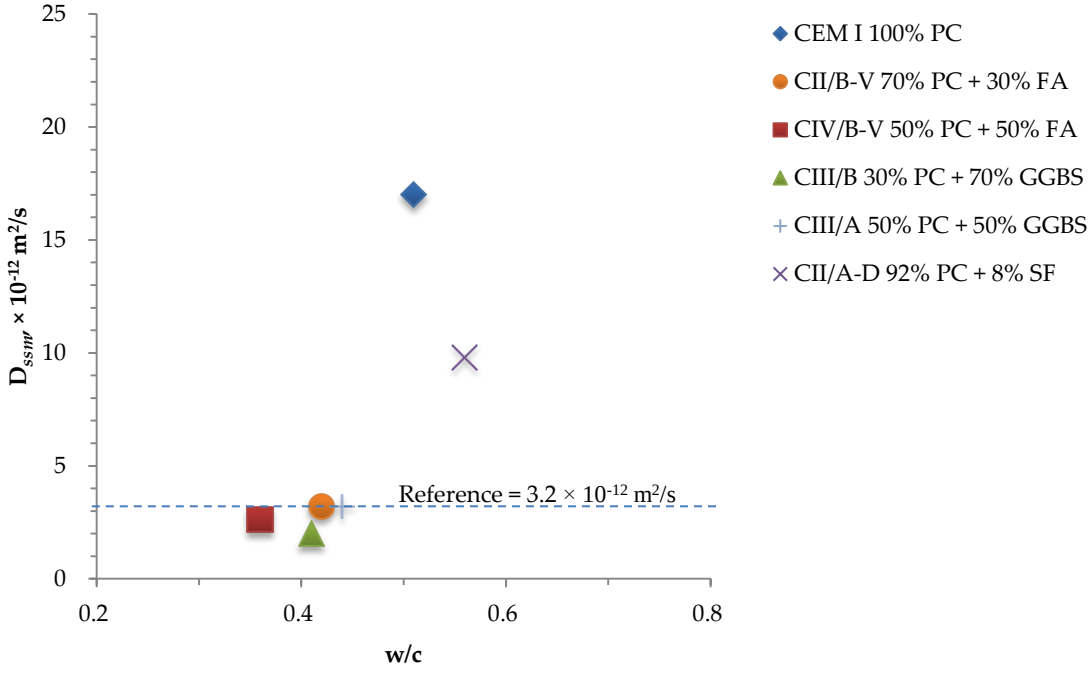


Figure 6.10 **Equivalent performance of concrete, 40 N/mm², 50 weeks, Multi-regime**

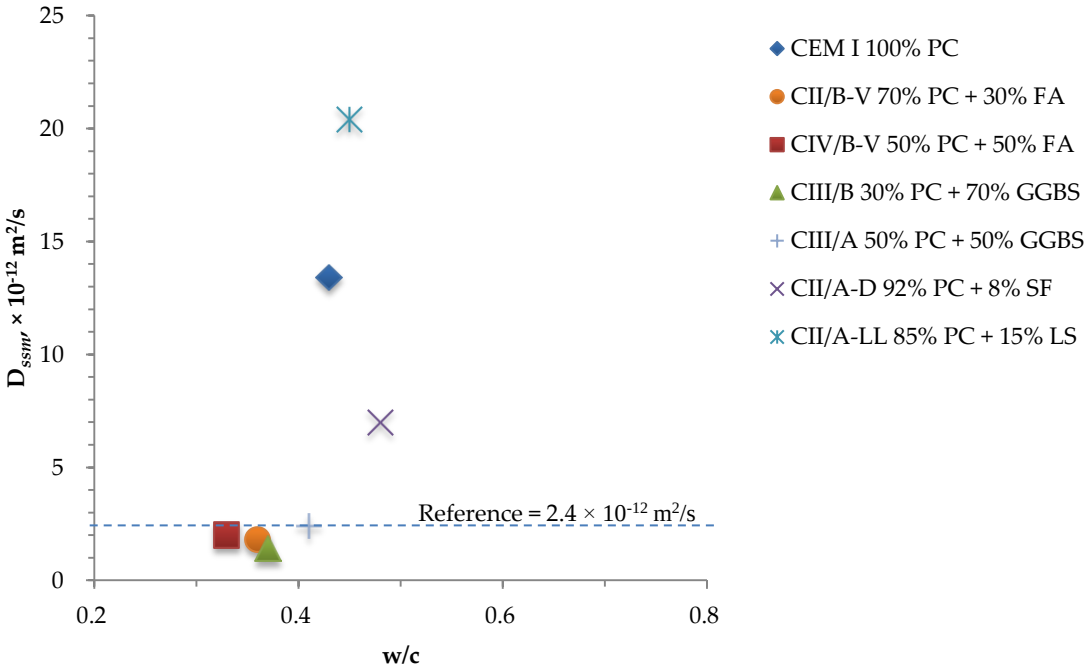


Figure 6.11 **Equivalent performance of concrete, 50 N/mm², 50 weeks, Multi-regime**

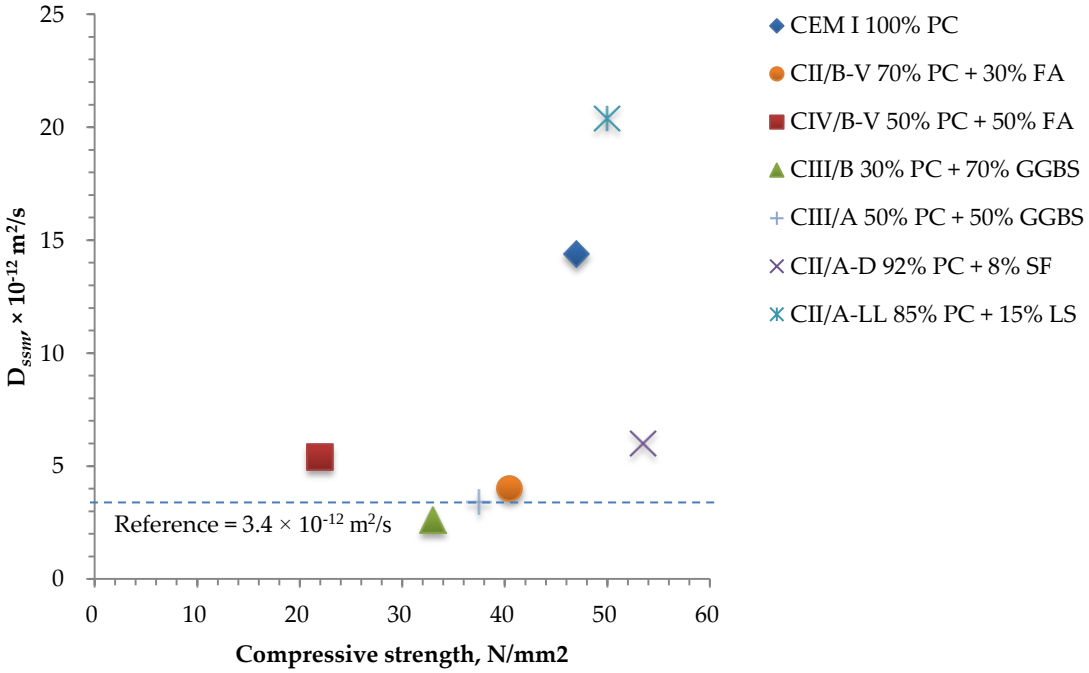


Figure 6.12 **Equivalent performance of concrete, 0.45 w/c, 50 weeks, Multi-regime**

Table 6.1 Normalised non-steady state D_{ssm} values of the test concrete mixes against the benchmark using the Multi-regime exposure method

Normalised mixes		20 weeks D_{ssm}, $\times 10^{-12}$ m²/s		
Mix code	EN 197 notation	40 N/mm²	50 N/mm²	0.45 w/c
N1	CEM I	22.2	18	19
N2	CII/B-V	3	1.8	3.6
N3	CIV/B-V	7.4	5.6	11.8
N4	CIII/A	3.2	2.6	3.4
N5	CIII/B	2.2	1.6	2.8
N6	CII/A-D	8.2	5.8	5
N7	CII/A-LL	-[A]	22.8	22.8

Normalised mixes		50 weeks D_{ssm}, $\times 10^{-12}$ m²/s		
Mix code	EN 197 notation	40 N/mm²	50 N/mm²	0.45 w/c
N1	CEM I	17	13.4	14.4
N2	CII/B-V	3.2	1.8	4
N3	CIV/B-V	2.6	2	5.4
N4	CIII/A	3.2	2.4	3.4
N5	CIII/B	2	1.4	2.6
N6	CII/A-D	9.8	7	6
N7	CII/A-LL	-	20.4	20.4

Note:
Reference mix = N4; indicated in the box
[A] denotes D_{ssm} value > 25×10^{-12} m²/s

CHAPTER 7. COMPARISON OF DURABILITY PERFORMANCE AND RANKING BETWEEN CEN TS 12390-11:2010, NT BUILD 492 AND MULTI-REGIME TEST.

7.1 INTRODUCTION

In this section, the diffusion coefficient from the CEN candidate test is compared with diffusion coefficient values from a rapid test standardised in the Nordic countries and a steady-state test standardised in Spain. The performance of these tests is not compared directly although the relationship of NT Build 492 and the sister test (NT Build 443) has been suggested by Tang and Basheer, (2007).

7.2 METHOD

The CEN TS 12390-11:2010 is compared with other tests that take a significantly shorter time to perform. Comparison is made on the ranking of concrete at equal age of 20 weeks and 50 weeks with all 3 test methods. The normalised diffusion coefficient D (non steady-state diffusion, non steady-state migration and steady-state migration) from each normalised elements namely 40 N/mm^2 and 50 N/mm^2 compressive strengths and 0.45 water-cement ratio are arranged against each tests methods and the rank order is observed.

In this regard the D values listed in the preceding figures are not separated although they represented different transport coefficients. The focus is the ranking of concrete and the magnitude of difference between all test methods.

A similar rank order across different tests suggests that with regards to comparative performance, a faster test has greater practicality in allowing greater flexibility in engineering decisions with regards to choosing or comparing different candidate mixes for chloride durability.

Equivalent performance is shown only up to 25×10^{-12} m^2/s. Values above that are considered to indicate that the concrete is unsuitable for chloride resistance.

In order to determine the precision on the test, the standard deviation of test results and their respective repeatability coefficient of variation are calculated. For this thesis, the mean coefficient of variation for CEN TS 12390-11:2010, NT Build 492 and Multi-regime was calculated as 27%, 12% and 17% respectively.

With the precision of test considered, the magnitude error of the test method can be approximated. As an example, taking the reference value of 2×10^{-12} m^2/s, the error for CEN TS 12390-11:2010 is

between 1.46 × 10^{-12} m^2/s to 2.54× 10^{-12} m^2/s, NT Build 492 is between 1.76 × 10^{12} m^2/s to 2.24 × 10^{-12} m^2/s and Multi-regime is between 1.66 × 10^{-12} m^2/s to 2.34 × 10^{-12} m^2/s.

7.3 EQUIVALENT DURABILITY PERFORMANCE COMPARISON AT 20 WEEKS

7.3.1 Normalised equal strength of 40 N/mm²

Figure 7.1 shows the performance and rank order of concretes at an equal strength of 40 N/mm². It can be seen that there is no result for limestone mix and CEM I for CEN TS 12390-11:2010 and NT Build 492. Taking into account test errors, there is no difference between both ggbs mixes for all 3 test methods. The range of D values are small, ranging between 1.6 × 10^{-12} m^2/s to 3.8 × 10^{-12} m^2/s, a difference of 2.2 × 10^{-12} m^2/s. Ranking between CEN TS 12390-11:2010 and Multi-regime is close, changing only for the CII/B-V mix with almost 60% reduction in the multi-regime test from 7.2 × 10^{-12} m^2/s to 3 × 10^{-12} m^2/s.

NT Build 492 shows a different ranking order for CII/A-D, CIV/B-V and CII/B-V mixes from the other 2 tests although taking into account the test error of 12%, these 3 mixes overlap each other.

7.3.2 Normalised equal strength of 50 N/mm²

Figure 7.2 shows the performance and rank order of concretes at an equal strength of 50 N/mm². The ranking of CII/A-D mix changed substantially at this strength from 10.8 × 10^{-12} m^2/s at 40 N/mm² to 5 × 10^{-12} m^2/s for CEN TS 12390-11:2010. However, other methods does not show change in ranking from 40 N/mm² to 50 N/mm².

7.3.3 Normalised equal water-cement ratio of 0.45

Figure 7.3 shows the performance and rank order of concretes at an equal water-cement ratio of 0.45. This follows the same ranking score for 50 N/mm² with almost similar magnitude for CEN TS 12390-11:2010. The same could also be said for the NT Build 492 test method.

The poor performance of CIV/B-V mix for Multi-regime test at the equal water-cement ratio of 0.45 may be explained by the low compressive strength of 22.0 N/mm² at the water-cement ratio of 0.45. CII/A-D mix has the highest compressive strength of 53.5 N/mm² at the equal water-cement ratio of 0.45 while its water -cement ratio at 40 N/mm² and 50 N/mm² is 0.56 and 0.48 respectively. This has contributed to the lowest D value attained in comparison with its D values at 40 N/mm² and 50 N/mm². This result is consistent in all test methods.

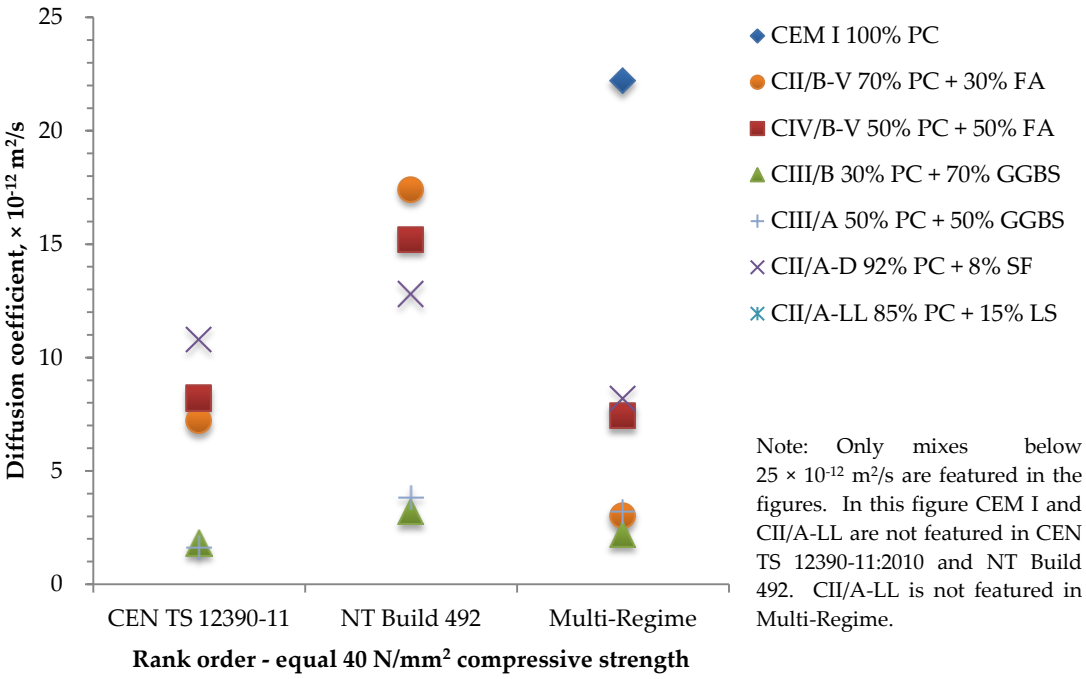


Figure 7.1 Performance and rank order of cements, 40 N/mm², 20 weeks

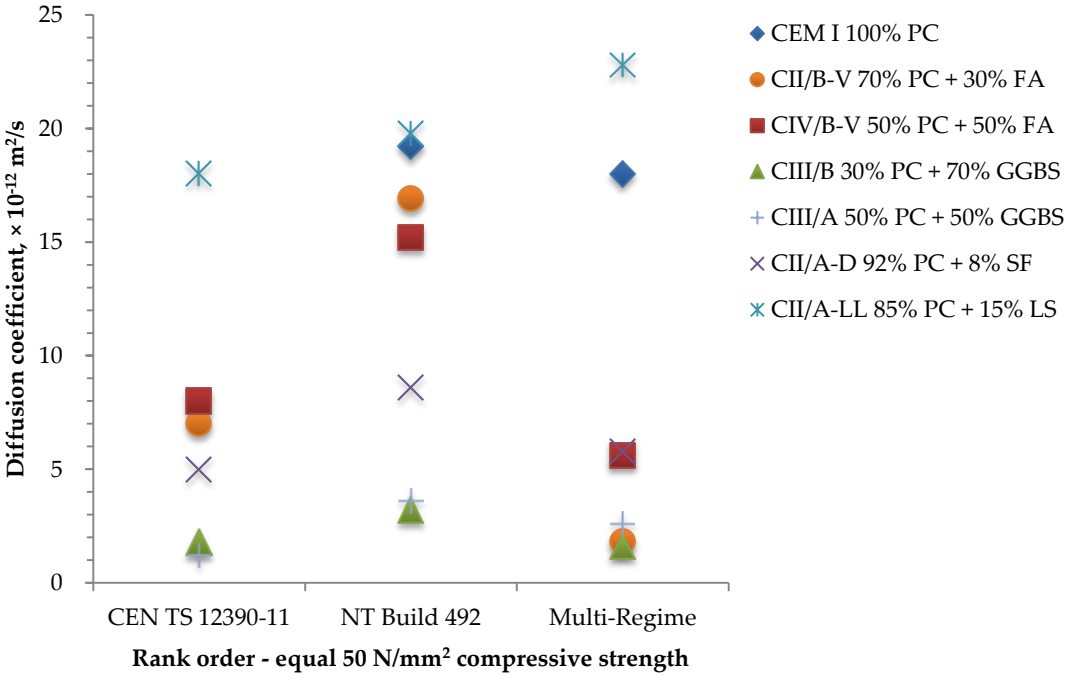


Figure 7.2 Performance and rank order of cements, 50 N/mm², 20 weeks

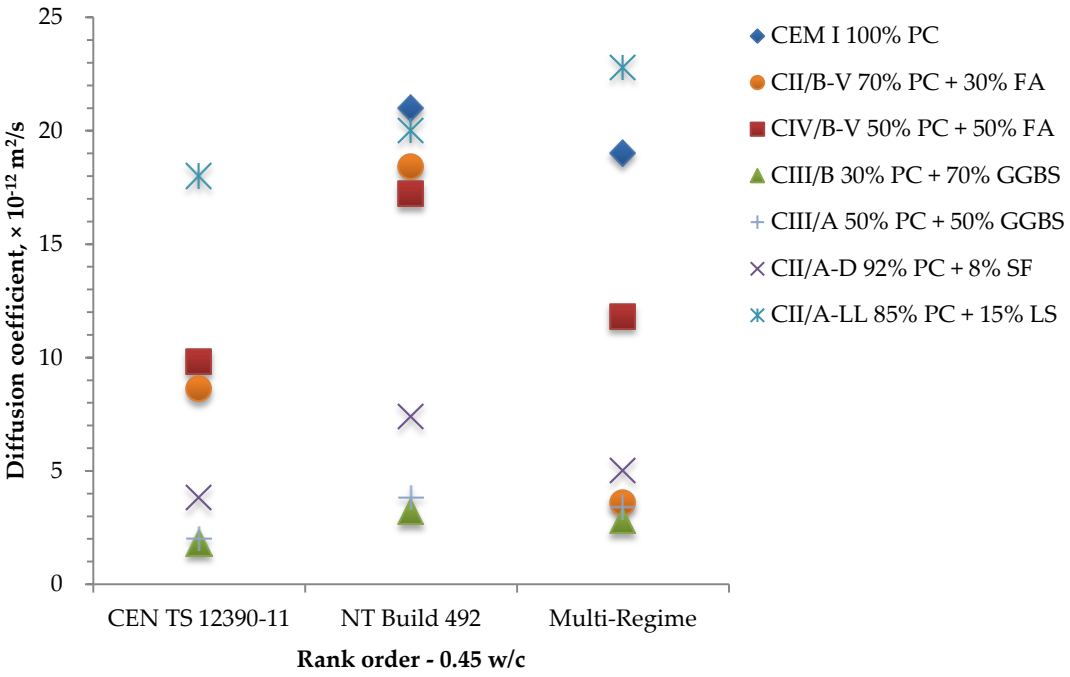


Figure 7.3 Performance and rank order of cements, 0.45 w/c, 20 weeks

7.4 EQUIVALENT DURABILITY PERFORMANCE COMPARISON AT 50 WEEKS

7.4.1 Normalised equal strength of 40 N/mm²

Figure 7.4 shows the performance and rank order of cements at an equal strength of 40 N/mm². The magnitude of difference between D values of all mixes is narrow where everything is below 5 × 10^{-12} m²/s except for CII/A-LL for CEN TS 12390-11:2010. CEM I is not featured.

NT Build 492 constantly has the highest typical D value amongst the 3 test methods. This is true for almost all mixes except CEM I where the highest D is biased towards the CEN TS 12390-11:2010 and CII/A-LL where its highest D is biased towards Multi-regime. The ranking for NT Build 492 is almost similar with CEN TS 12390-11:2010 where there is a change of ranking between both fly ash mixes at the middle of the rank order.

The Multi regime test at the normalised equal strength of 40 N/mm² shows that all ggbs and fly ash mixes are very close together with D values between 3.2 × 10^{-12} m²/s and 2.0 × 10^{-12} m²/s. The best performing mix is CIII/B followed by CIV/B-V at 2.6 × 10^{-12} m²/s while CII/B-V and CIII/A returns a similar D value of 3.2 × 10^{-12} m²/s. CII/A-D mix with the highest water-cement ratio at this equal age is the next at 9.8 × 10^{-12} m²/s.

Table 7.1 shows the rank order between 20 weeks and 50 weeks changed for all test methods but in general terms the rank order for all test methods according to cement performance is ggbs> fly ash> silica fume> CEM I> CII/A-LL.

7.4.2 Normalised equal strength of 50 N/mm²

Figure 7.5 shows the performance and rank order of cements at an equal strength of 50 N/mm². Similar to the 20 weeks normalisation, the ranking of CII/A-D mix changed from worse than the fly ash mixes at 40 N/mm² to better than the fly ash mixes at 50 N/mm² for CEN TS 12390-11:2010.

The water-cement ratio for CII/A-D is still higher for the equal strength at 0.48 compared to 0.33 and 0.36 for CIV/B-V and CII/B-V respectively. This may suggest that the fly ash mix has nearly reached the ceiling of improvement at their water-cement ratio whilst for CII/A-D it can hypothetically still improve. Indeed, studying the 0.45 water-cement ratio performance of CII/A-D mixes on all test methods shows that they are better still.

Between 40 N/mm² and 50 N/mm², the ranking of mixes is the same for NT build 492. However, the magnitude of D value is different especially for the CII/A-D mix. Carrying on from the theme

of improvement of D value as water-cement ratio drops, NT build test shows that it visualises the improvement more that other test methods in this thesis.

The switch between the rankings of the 2 fly ash mixes is still visible for CEN TS 12390-11:2010 and NT Build 492 in the middle of the rank order. Given the precision of the test, however, and the proximity of D values for CEN TS 12390-11:2010 it could be argued that there could be no difference between the position of both fly ash mixes.

The CIV/B-V mix is shown to be still improving for Multi-regime test compared to the 20 weeks 50 N/mm^2 D value. Other mixes are also improving but at a more modest rate. Referring back to Table 6.1 shows that CIV/B-V reduces from 5.6 × 10^{-12} m^2/s to 2.0 × 10^{-12} m^2/s, a 64% improvement. Other mixes for the group i.e. CIII/A, CIII/B and reduces by 0.2 × 10^{-12} m^2/s whilst CII/B-V does not change. Table 7.2 shows the change in ranking from 20 weeks to 50 weeks for mixes normalised to 50 N/mm^2 comprassive strength.

7.4.3 Normalised equal water-cement ratio of 0.45

Figure 7.6 shows the performance and rank order of cements at an equal water-cement ratio of 0.45. The CII/A-D cement at this water-cement ratio has higher compressive strength (53.5 N/mm^2). Subsequently its D value is lower than the previous 2 comparison based on equal compressive strength in CEN TS 12390-11:2010 of 40 N/mm^2 and 50 N/mm^2 where its water-cement ratio is 0.56 and 0.48 respectively. Therefore this supports the argument of a gradual exponential limitation to D value improvement as water-cement ratio reduces. Ranking for the CEN TS 12390-11:2010 is –from best to worse- CIII/B> CIII/A> CII/A-D> CII/B-V and CIV/B-V. CII/A-LL and CEM I may be considered unsuitable for the chloride environment.

Ranking for NT build 492 with the same mixes changed from the CEN TS 12390-11:2010 method. CIII/B and CIII/A still come out the best but CII/A-D, CII/B-V and CIV/B-V have swapped position between each other. It is interesting to note that the CIV/B-V mix which has the lowest compressive strength at this water-cement ratio (22 N/mm^2) has better performance than the CII/B-V and the CII/A-D mixes with 40.5 N/mm^2 and 53.5 N/mm^2 respectively.

The multi-regime test method is more similar to the CEN TS 12390-11:2010 in terms of ranking. The position of CII/A-D mix has changed so the ranking is –from best to worse- CIII/B> CIII/A> CIV/B-V> CII/B-V and CII/A-D.

The change in ranking from 20 weeks to 50 weeks for all tests are shown in Table 7.3 for normalised mixes at equal water/cement ratio of 0.45.

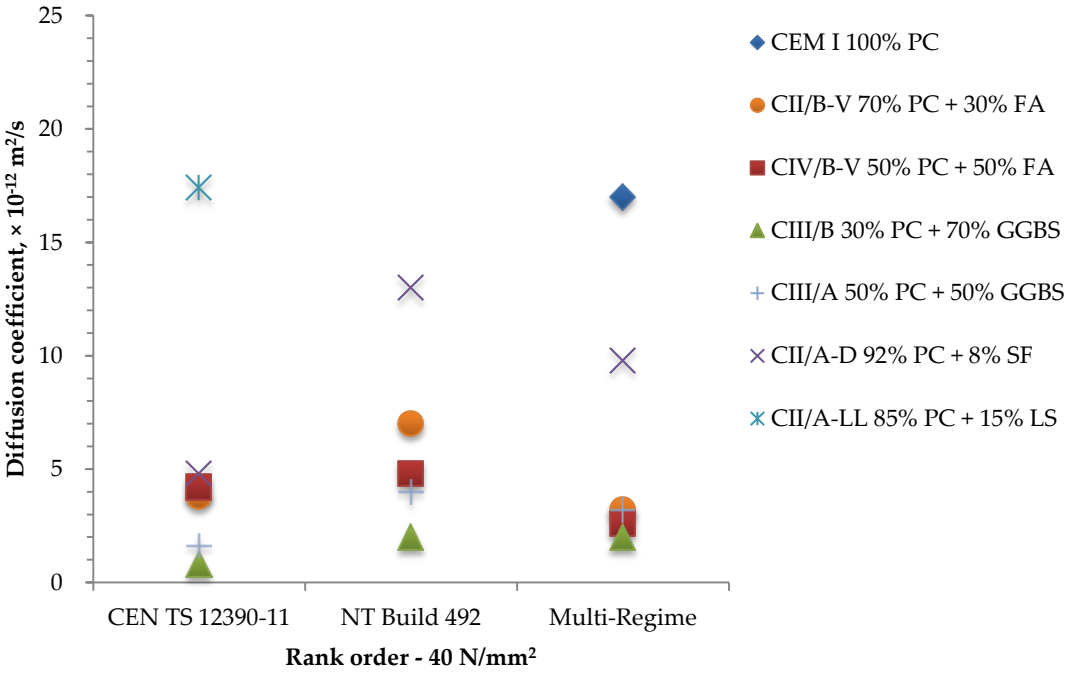


Figure 7.4 **Performance and rank order of cements, 40 N/mm², 50 weeks**

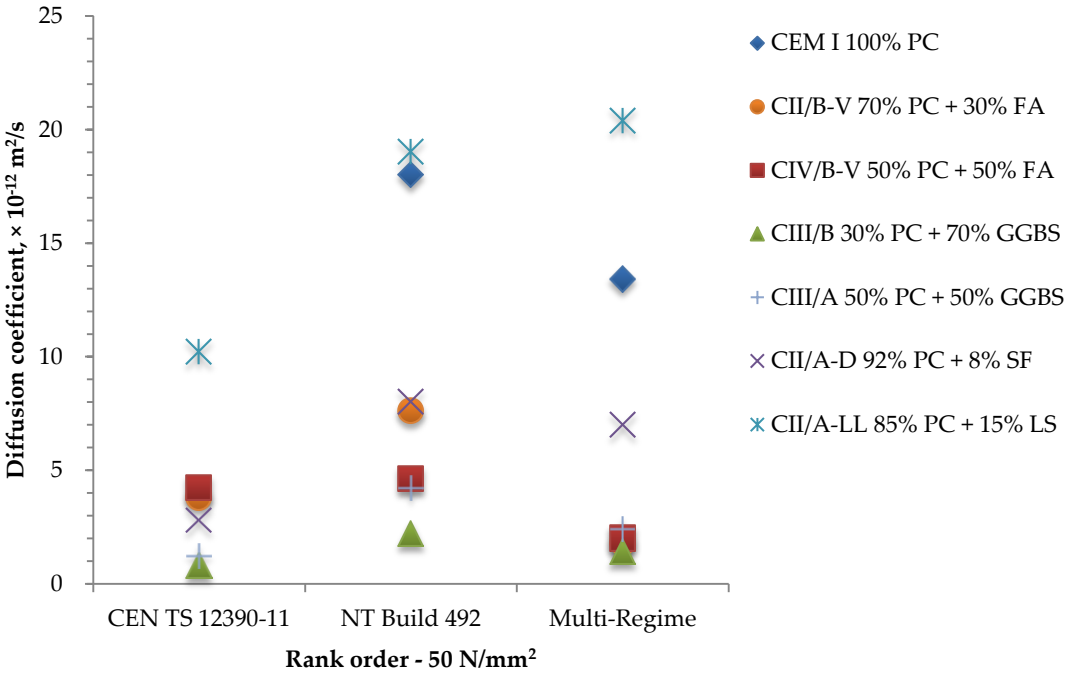


Figure 7.5 **Performance and rank order of cements, 50 N/mm², 50 weeks**

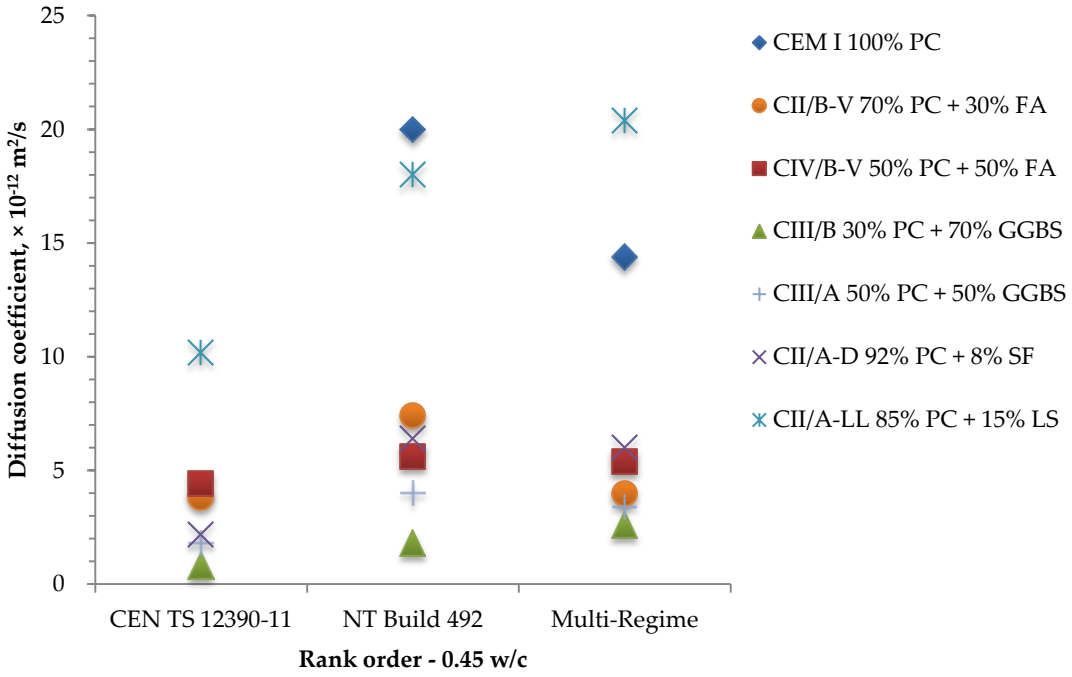


Figure 7.6 Performance and rank order of cements, 0.45 w/c, 50 weeks

Table 7.1 Change of rankings for mixes normalised to 40 N/mm² between 20 to 50 weeks

Ranking, best to worse	CEN TS 12390-11:2010		Change	NT Build 492		Change	Multi-regime		Change
	20 weeks	50 weeks		20 weeks	50 weeks		20 weeks	50 weeks	
1	CIII/A	CIII/B	↑	CIII/B	CIII/B	–	CIII/B	CIII/B	–
2	CIII/B	CIII/A	↓	CIII/A	CIII/A	–	CII/B-V	CIV/B-V	↑
3	CII/B-V	CII/B-V	–	CII/A-D	CIV/B-V	↑	CIII/A	CII/B-V	↓
4	CII/A-D	CII/A-D	–	CIV/B-V	CII/B-V	↑	CIV/B-V	CIII/A	↓
5		CII/A-LL		CII/B-V	CII/A-D	↓	CII/A-D	CII/A-D	–
6							CEM I	CEM I	–
7									

Note:

↑ Up, ↓ Down, – Not moving

Table 7.2 Change of rankings for mixes normalised to 50 N/mm² between 20 to 50 weeks

Ranking, best to worse	CEN TS 12390-11:2010		Change	NT Build 492		Change	Multi-regime		Change
	20 weeks	50 weeks		20 weeks	50 weeks		20 weeks	50 weeks	
1	CIII/A	CIII/B	↑	CIII/B	CIII/B	–	CIII/B	CIII/B	–
2	CIII/B	CIII/A	↓	CIII/A	CIII/A	–	CII/B-V	CIV/B-V	↑
3	CII/A-D	CII/A-D	–	CII/A-D	CIV/B-V	↑	CIII/A	CII/B-V	↓
4	CII/B-V	CII/B-V	–	CIV/B-V	CII/B-V	↑	CIV/B-V	CIII/A	↓
5	CIV/B-V	CIV/B-V	–	CII/B-V	CII/A-D	↓	CII/A-D	CII/A-D	–
6	CII/A-LL	CII/A-LL	–	CEM I	CEM I	–	CEM I	CEM I	–
7				CII/A-LL	CII/A-LL	–	CII/A-LL	CII/A-LL	–

Table 7.3 Change of rankings for mixes normalised to 0.45 water-cement ratio between 20 to 50 weeks

Ranking, best to worse	CEN TS 12390-11:2010		Change	NT Build 492		Change	Multi-regime		Change
	20 weeks	50 weeks		20 weeks	50 weeks		20 weeks	50 weeks	
1	CIII/A	CIII/B	↑	CIII/B	CIII/B	–	CIII/B	CIII/B	–
2	CIII/B	CIII/A	↓	CIII/A	CIII/A	–	CIII/A	CIII/A	–
3	CII/A-D	CII/A-D	–	CII/A-D	CIV/B-V	↑	CII/B-V	CII/B-V	–
4	CII/B-V	CII/B-V	–	CIV/B-V	CII/A-D	↓	CII/A-D	CIV/B-V	↑
5	CIV/B-V	CIV/B-V	–	CII/B-V	CII/B-V	–	CIV/B-V	CII/A-D	↓
6	CII/A-LL	CII/A-LL	–	CII/A-LL	CII/A-LL	–	CEM I	CEM I	–
7				CEM I	CEM I	–	CII/A-LL	CII/A-LL	–

Note:

↑ Up, ↓ Down, – Not moving

7.5 OBSERVATIONS

The ranking comparison shows that there is a limit to the lowering of water-cement ratio to increase durability performance. As it stands, all 3 test methods show the same effect.

As strength and age increases it became harder to differentiate performance as mixes expected to perform well in chloride environment gets closer together. At 50 weeks 0.45 water-cement ratio the Multi-regime test methods and CEN TS2390-11 return the narrowest magnitude range in ranking especially mixes under 5×10^{-12} m²/s (3.4×10^{-12} m²/s vs. 3.6×10^{-12} m²/s difference respectively) whilst NT Build 492 has a difference of 6.4×10^{-12} m²/s). This shows that NT Build 492 is more sensitive to differences in ranking. Furthermore, given the precision of each of the test methods, at the narrower range, performance of different mixes started to overlap.

The ranking of concrete with the non steady-state tests i.e. CEN TS 12390-11:2010 and NT Build 492 is relatively similar for all normalisations at both test age of 20 weeks and 50 weeks. They follow the pattern of ggbs> fly ash and silica fume (on equal 50 N/mm² and 0.45 water-cement ratio, silica fume is better with CEN TS12390-11)> limestone> CEM I.

The ranking from the steady-state multi-regime test is different at all ages and normalisation. However, they follow the sequence of ggbs and fly ash (these are interchangeable)> silica fume> CEM I and limestone.

The magnitude difference of D values change from 20 weeks to 50 weeks and are highest for the NT Build 492 test. The changes in the ranking order were noted for mixes that performs below 25.0×10^{-12} m²/s especially those with fly ash. Fly ash improved by 68% from 16.7×10^{-12} m²/s to 6.2×10^{-12} m²/s. This supports the argument that testing concrete at an early age will require a different age factor. However, for different test methods the ageing factor will not be the same. This is illustrated when in comparison, CEN TS 12390-11:2010 shows only 51% average improvement from 8.1×10^{-12} m²/s to 4×10^{-12} m²/s.

CHAPTER 8. FURTHER INVESTIGATIONS ON CEN TS 12390-11:2010 TEST METHOD

8.1 OVERLAY OF RESULTS AGAINST CONCRETE SOCIETY TECHNICAL REPORT 61

8.1.1 Introduction

The Concrete Society published a Technical Report in 2004 (CSTR61) as a guidance for minimising the risk of corrosion reinforcement in concrete (Bamforth, 2004). This publication includes a predictive model for chloride induced corrosion and within it ageing parameters for different concrete types based on an extensive set of data. The non steady-state diffusion values calculated during the study, was similar to the method used in this publication, which was based on Fick's second law. The empirical ageing factors determined through this report based on the slope of log-log plot relationship of D_{nss} value vs. time are as follows:

CEM I concretes	-0.264
fly ash concretes	-0.699
ggbs concretes	-0.621
silica fume	the age factor for silica fume concrete appears to be related to the water-cement ratio of the mix. The age factor and the age factor n is described by the equation: $n = -1 + 1.10(\mathrm{w/c})$

The ageing factor proposed by the report did not take into account the concrete mix proportions, water-cement ratio or materials sources and according to Bamforth, (1996), these factors account for much of the scatter. However, the ageing trend is quite apparent. The D_{nss} values obtained in the experimental programme are overlaid against the ageing factor plots from the Concrete Society Technical Report 61.

8.1.2 Results

Figure 8.1 to Figure 8.4 show the result of the overlay and the ageing factor obtained as defined by the slope of the log-log relationship of D_{nss} value vs. time (years) for the data from this thesis:

CEM I concretes	-0.142
fly ash concretes	-0.774
ggbs concretes	-0.437
silica fume	the age factor for silica fume concrete still follows the equation: $n = -1 + 1.10(\mathrm{w/c})$ for the 0.4 water-cement ratio

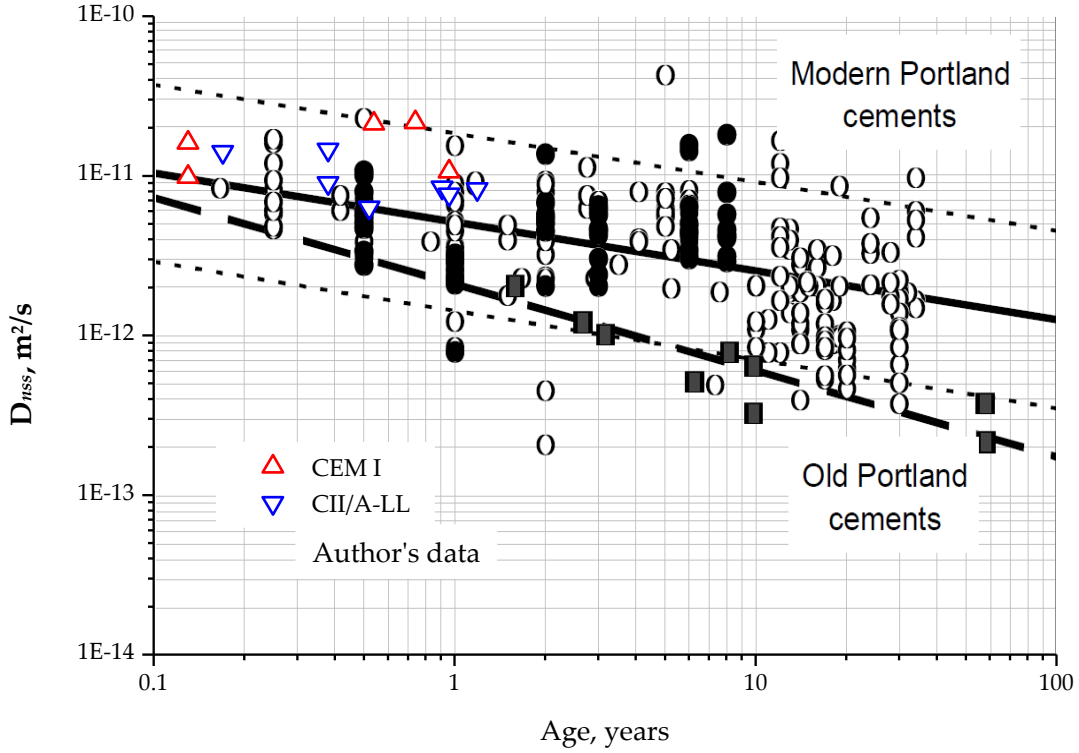


Figure 8.1 **Age dependent values of D_{nss} and the data in CSTR61 used to derive the age factor for CEM I concrete and the overlay of thesis data in colour**

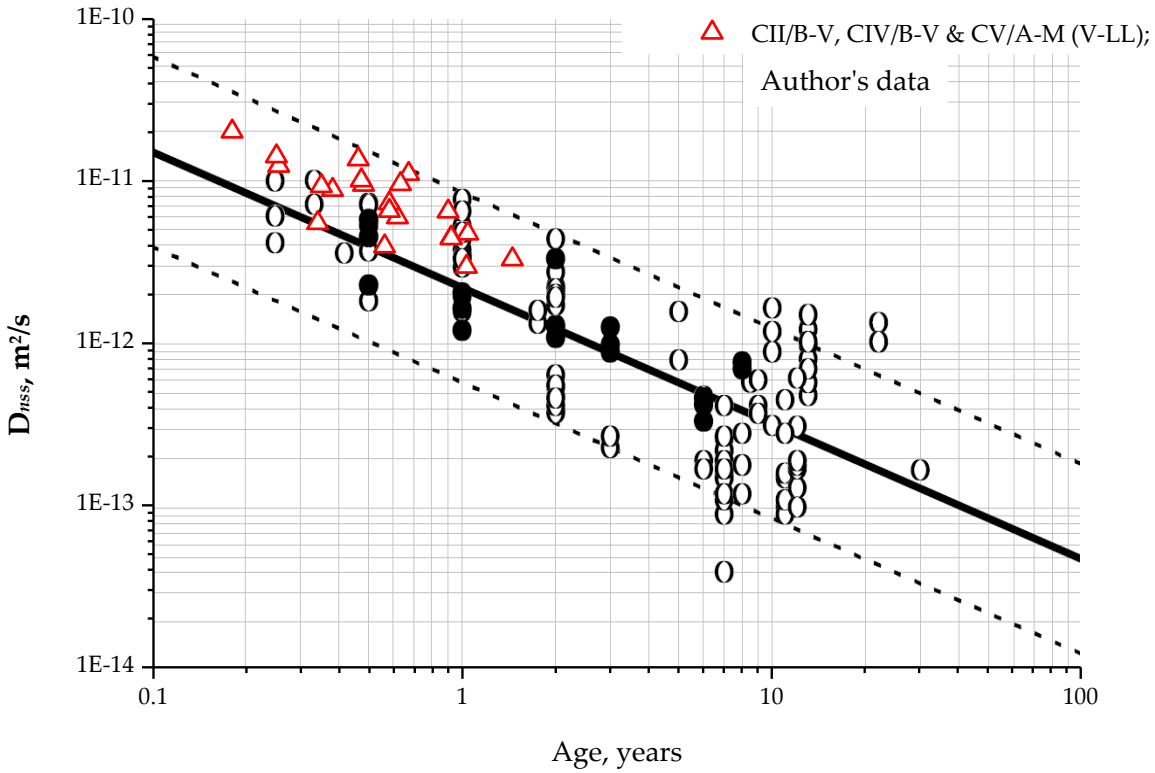


Figure 8.2 **Age dependent values of D_{nss} and the data in CSTR61 used to derive the age factor for fly ash concrete and the overlay of thesis data in colour**

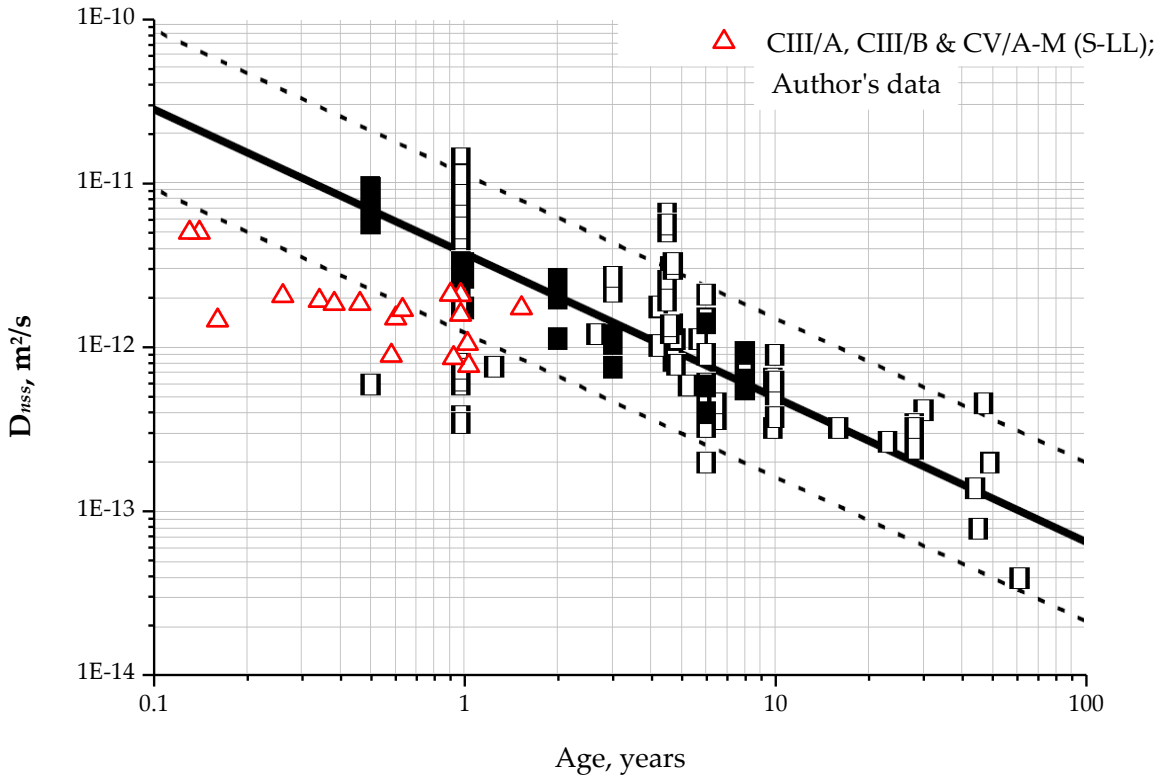


Figure 8.3 **Age dependent values of D_{nss} and the data in CSTR61 used to derive the age factor for ggbs concrete and the overlay of thesis data in colour**

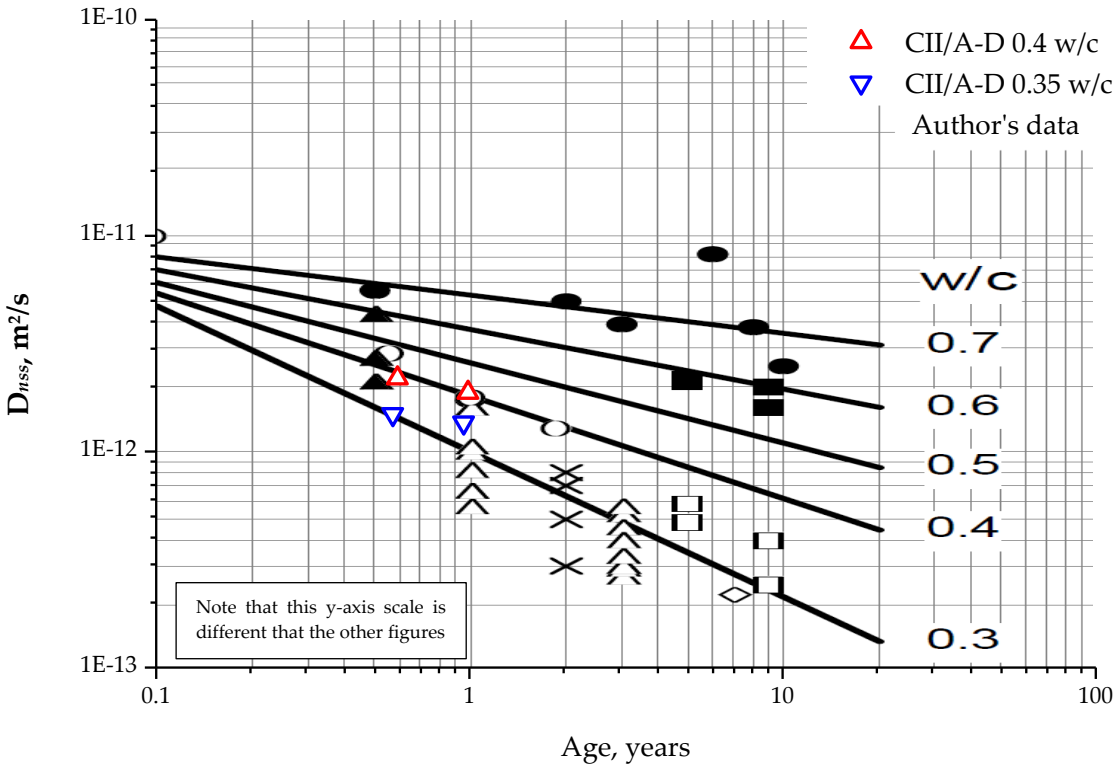


Figure 8.4 **Age dependent values of D_{nss} and the data in CSTR61 used to derive the age factor for silica fume concrete and the overlay of thesis data in colour**

8.1.3 Observations

Looking at the age exponent measured from the thesis data exclusively, shows that the ageing factor from this thesis is different from the ageing factor derived from the technical report. However, when the data were overlaid over the age exponent data from the technical report they show that most of the data points complemented the existing data.

CEM I and CII/A-LL exponent fell within the 95% confidence level of the data presented. The limestone mixes were included in the CEM I exponent data because they were regarded as inert filler. Similarly, fly ash and ggbs concrete mixes with limestone replacements were grouped in their respective groups, either fly ash or ggbs.

The fly ash mixes fitted perfectly within the 95% confidence level from the technical report. The difference between the exponent data by Bamforth and the thesis is only 0.075. The ggbs concrete shows a decrease of 30% from the ageing exponent indicated by the technical report. The D_{nss} values for this thesis in Figure 8.3 are lower at the early age compared to the data presented by the ageing exponent. According to Harrison, (2012), the difference may be due to the increasing quality of ggbs cement. It is now possible to achieve the same 28 days compressive strength with 50% ggbs replacement due to the current market needs.

It was also found that the ageing exponent for the silica fume concretes especially for the 0.4 water-cement ratio fits well with recommendation and the 0.35 water-cement ratio silica fume is in-between the exponent for 0.3 and 0.4 water-cement ratio concrete.

This exercise reveals an important point, the test method fits the diffusion coefficient of environmental exposure at least for around 1 year, as a lot of data from the ageing exponent for the technical report was obtained from external exposure conditions. Secondly, the ageing exponent is a dynamic factor as it may change with the change in cement quality and continual update of data is needed to account for this change.

It is acknowledged that a practical problem with the ageing factor proposed by CSTR 61 is that the confidence limit is too wide with a lot of scatter in the data. However, the discussion on the accuracy of the ageing factor of the technical report is outside the scope of this thesis.

8.2 PROGRESS OF CHLORIDE DIFFUSION IN THE CEN TS 12390-11:2010 TEST METHOD

8.2.1 Introduction

The test method specifies that the test is carried out over 90 day period in 3% sodium chloride solution. However, the test specification allows variation with respect to other concentration or solutions and different exposure periods. It is of interest to the test community that the effects of these variations are known.

This section is concerning one of the allowed variation to the test specification. It was believed that the variation of different exposure concentration and different exposure solution for example testing with artificial seawater will yield an incomparable result to the original specification anyway. It was therefore decided to focus the investigation on the effects of different exposure period as this parameter may easily be changed or the profile grinding date missed during the long test period.

Three mix types were chosen for this purpose. They are CII/A-LL, CII/B-V and CIII/A. The water-cement ratio for each mix is 0.4, 0.5 and 0.5 respectively. CII/A-LL was chosen because it represents concrete with limited chloride binding capacity whilst the other two cement types represents concretes with different chloride binding capacities. Together, the three cement types give a range of chloride from low to high levels. The age of the concrete at the start of testing was 76 weeks, 79 weeks and 62 weeks for CII/B-V, CIII/A and CII/A-LL respectively. The difference in age is not suspected to be significant as at these ages the effect of ageing can be assumed for all concrete has relatively stabilised.

The focus is therefore on evolution of the D_{nss} value during the test period and the effects of tests less than and longer than 90 days.

8.2.2 Method

These concretes were the same concrete used in the main test programme. Instead of only 90 days of test exposure period, they were tested for 30 days, 60 days, 90 days and 120 days. Other parameters of the test i.e. exposure concentration, solution, volume and exposure environment remain the same. The test specimen preparation was followed as per the CEN TS 12390-11:2010 document as well as the treatment after the end of the test with profile grinding and acid soluble chloride determination. The test was done on duplicate cube specimens for each test and the results show the average.

8.2.3 Results

Figure 8.5 shows the evolution of D_{nss} value measured over the test period of 120 days. It can be seen that the CII/B-V mix has the highest rate of decay followed by the CIII/A mix. The CII/A-LL mix fluctuates within 2×10^{-12} m^2/s over the 120 days period reflecting the assumption of low binding capacity.

Table 8.1 shows that the CIII/A mix has a higher calculated C_s in general compared to either the CII/B-V or the CII/A-LL. The concentration of chloride near the surface for CIII/A mix is also higher than that of CII/B-V mix.

Comparatively the amount of chloride that enters the specimen is reflective of the D_{nss} value measured. In order to elucidate this point, chloride concentration was checked at the end of the 120 days test and it was found that the drop in the level of exposure solution concentration is the inverse to the D_{nss} value obtained. The lower the final exposure solution concentration, the higher D_{nss} value measured. As an example, the CII/A-LL mix has a final chloride concentration of 2.93% and D_{nss} value of 8.41×10^{-12} m^2/s and the CIII/A mix has a final chloride concentration of 2.99% and D_{nss} value of 1.73×10^{-12} m^2/s.

8.2.4 Observations

These results indicates that the testing period of 90 days may be considered to be adequate for testing as D_{nss} value does not change significantly after. However, due to the limited number of tests conducted to observe this effect and the lack of published data on the subject, more tests will be needed to arrive at a significant conclusion especially tests that lasts longer, say 6 months or 1 year.

Even though the ggbs mix has a higher replacement level, the calculated aluminate content of the 50% ggbs mix (8.2% overall) is lower than the 30% fly ash mix (8.9% overall). This may explain the rate of reduction in D_{nss} value for fly ash which is better than that of the ggbs. Weight by weight, the fly ash used in this research has almost 40% more Al_2O_3 than ggbs.

However, since the ggbs mix has a higher C_s and high concentration on the near surface plane, may suggests chloride is bound more aggressively by the ggbs mix.

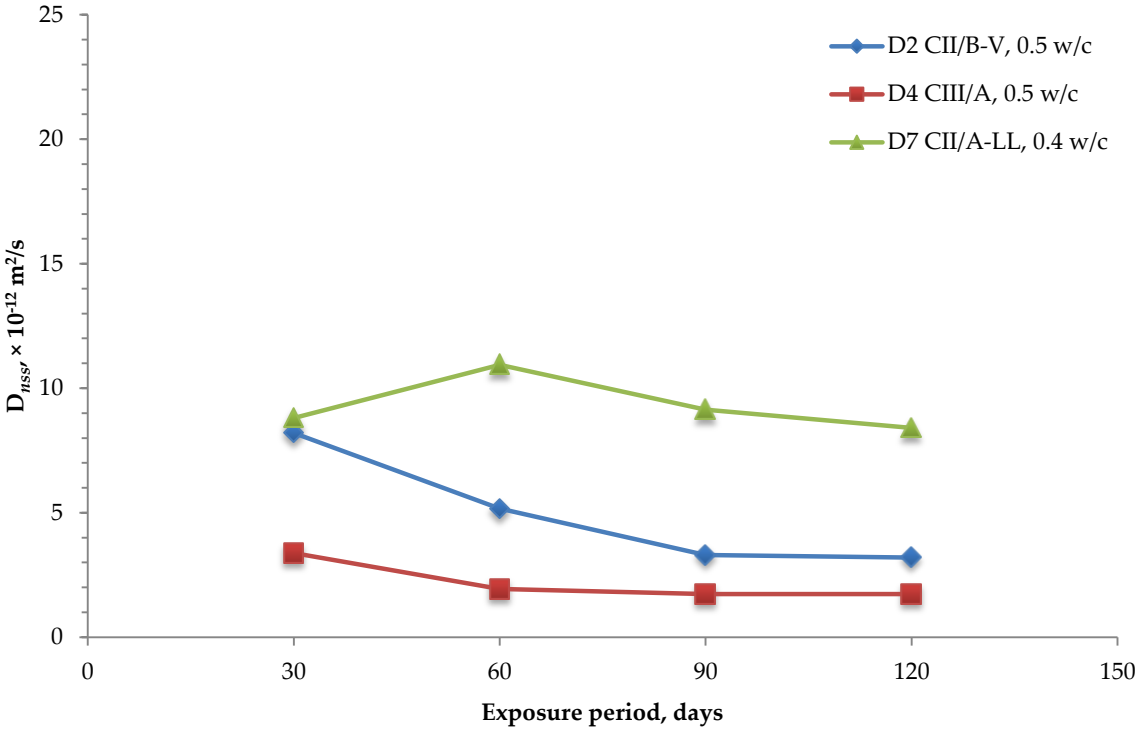


Figure 8.5 Evolution of the D_{nss} value over time for CEN TS 12390-11:2010

Table 8.1 Average D_{nss} value, C_s and total acid soluble chloride* for all concrete

Mix	Exposure period, Days	Diffusion coefficient D_{nss}, × 10^{-12} m^2/s	C_s, mass % concrete	Total acid soluble Cl, mass % concrete*
	30	8.20	0.39	1.01
CII/B-V 0.5 w/c	60	5.16	0.33	1.03
30% FA	90	3.30	0.36	1.08
	120	3.2	0.39	1.20
	30	3.38	0.51	0.91
CIII/A 0.5 w/c	60	1.93	0.50	0.99
50% ggbs	90	1.73	0.56	1.27
	120	1.73	0.83	1.38
	30	8.81	0.36	1.39
CII/A-LL 0.4 w/c	60	10.94	0.34	1.75
15% LS	90	9.14	0.38	2.04
	120	8.41	0.35	1.92

* Cumulative total of acid content of all profiled layers

8.3 EFFECTS OF ARTIFICIAL SEA WATER CYCLIC EXPOSURE ON THE CEN TS 12390-11:2010 TEST METHOD

8.3.1 Introduction

The ultimate aim of testing concrete with NaCl exposure is to estimate durability in real structures for real civil engineering challenges. A test programme involving site exposure was not possible in this case as University of Dundee does not have its own seawater exposure site. To circumvent this, tests in an artificial exposure environment were undertaken using tidal exposure tanks.

The aim of the test is to investigate the differences in testing with cut specimens in the laboratory with specimen with as-cast faces in the cyclic wetting and to find out whether skin effect particularly increased protection from brucite layer can be observed as proposed by several researchers.

8.3.2 Method

Selected XS3 classes mixes were exposed to an artificial tidal environment described in Section 3.6.5. The mixes and their exposure parameters are detailed in Table 8.2.

100 mm cube specimens with as-cast surface were exposed to the tidal cycle, the earlier specimens at the nominal period of 90 days but the later ones were exposed longer. This is because as the results for the first of the specimens came back, it was found that even with CEM I mix, chloride ingress is low. As a consequence, the later specimens were exposed even longer, up to about 6 months to allow for more diffusion to take place. Figure 8.6 shows profile from CEM I concrete at 90 days exposure and Figure 8.7 shows the profiles obtained from CIII/B concrete at 6 months exposure.

The surface layers of the specimens were tested for traces of Brucite using Hiltonbrooks XRD equipment and further identification with Rietveld analysis using Xfit software. There were negligible or no traces of brucite in the powdered surface samples tested.

8.3.3 Results

Figure 8.8 shows the result of all mixes exposed to the cyclic wetting and drying environment.

Compared to the standard exposure using cut specimens in NaCl only, it was observed that the profile of the mixes shows a relatively high surface concentration of chloride. This can be attributed to the as-cast surface of the concrete having higher paste content compared to the bulk concrete content thus providing more sites for the chloride to adhere to.

All concretes tested including CEM I mixes have performed better than concrete in standard NaCl exposure at an equal age although brucite content was negligible. The percentage difference varies between 90% to 16%. As the cyclic wetting test is significantly different from the reference test, not much can be interpreted from the comparison other than it shows that there are other mechanisms that limit chloride ingress in seawater exposure.

8.3.4 Observations

It was observed that throughout the exposure period, the concrete surface never dries out with the wetting and drying cycle of 6 hours wet and dry. This is despite the use of blower fan on the tank to circulate air in order to promote drying.

The XRD determination gave inconclusive evidence of brucite and this shows that brucite may or may not form on the surface of the concrete in this elevated chloride exposure. It was hoped that by increasing the concentration of the exposure solution to 1 molar, ion exchange at the concrete surface may be intensified and precipitation of the brucite skin may be enhanced. As the result show, the success of this attempt was limited.

Despite this test changing the solution concentration, it is still hard to get diffusion of chloride into the concrete. Indeed it has been suggested that chloride ingress in marine condition is limited due to the sulfate ion in seawater that compete with chloride ion for binding site (Zibara, 2001). The precipitate from sulfate binding reduces the pore space and the pathway for chloride ingress.

Service life models that rely on prediction made with data from standard NaCl exposure may be too conservative for marine exposure. It has to be pointed out that the pragmatic approach is for the bulk concrete to provide resistance to chloride ingress and not to rely on surface skin to provide protection.

Table 8.2 Specimens exposed in cyclic wetting tank

Mix code	EN 197 notation	Exposure duration, days
D1	CEM I 52,5 R	90
S1	CEM I 52,5 R	112
S2	CII/B-V	195
S3	CIV/B-V	195
S4	CIII/A	120
S5	CIII/B	195
S10	CV/A-M (S-LL)	89

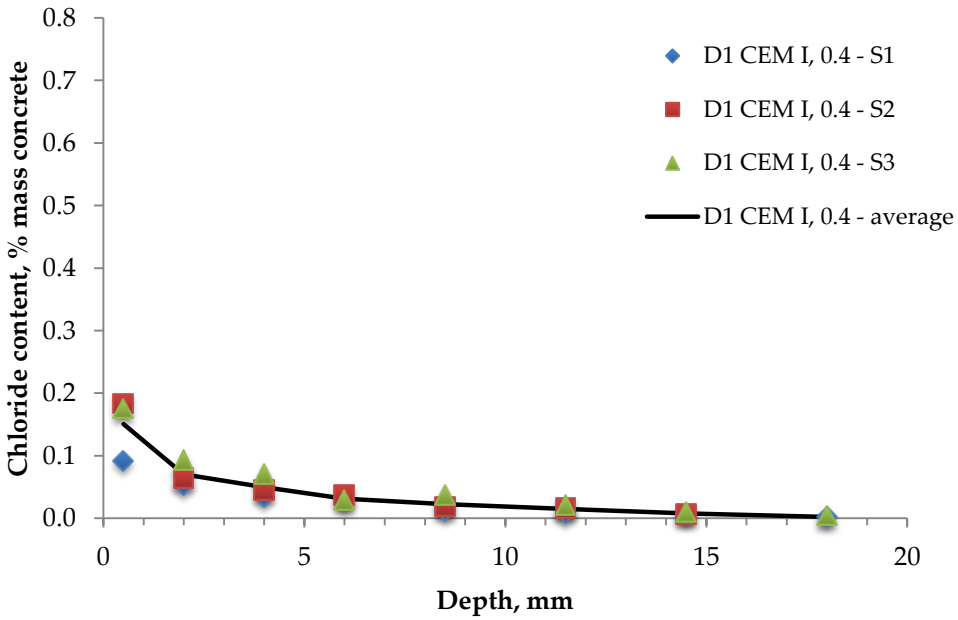


Figure 8.6 Chloride profile, mix D1, CEM I 0.4 w/c, 52 weeks age, 90 days exposure

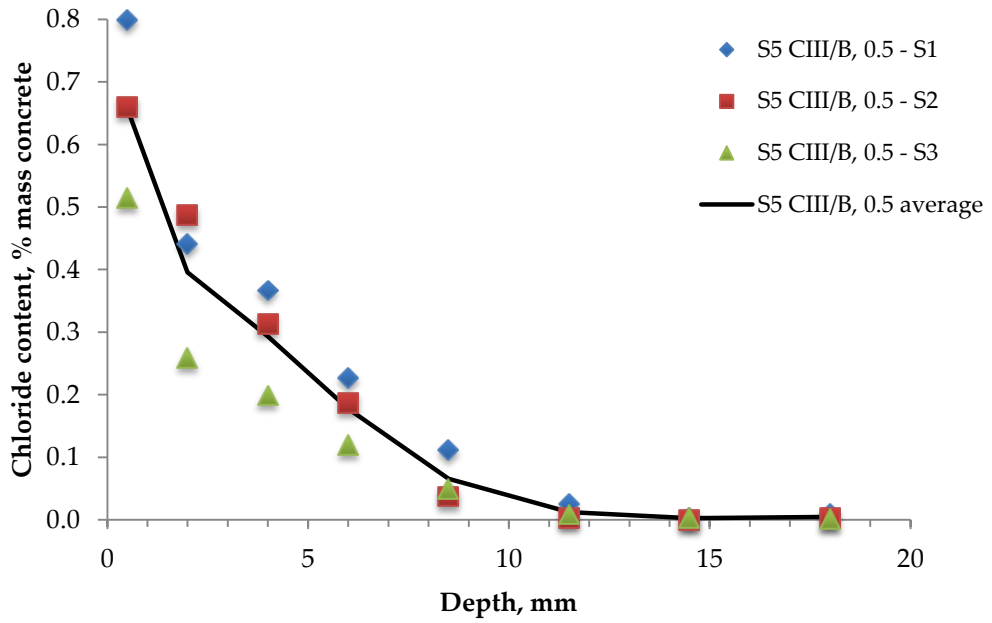


Figure 8.7 **Chloride profile, mix S5, CIII/B 0.5 w/c, 50 weeks age, 195 days exposure**

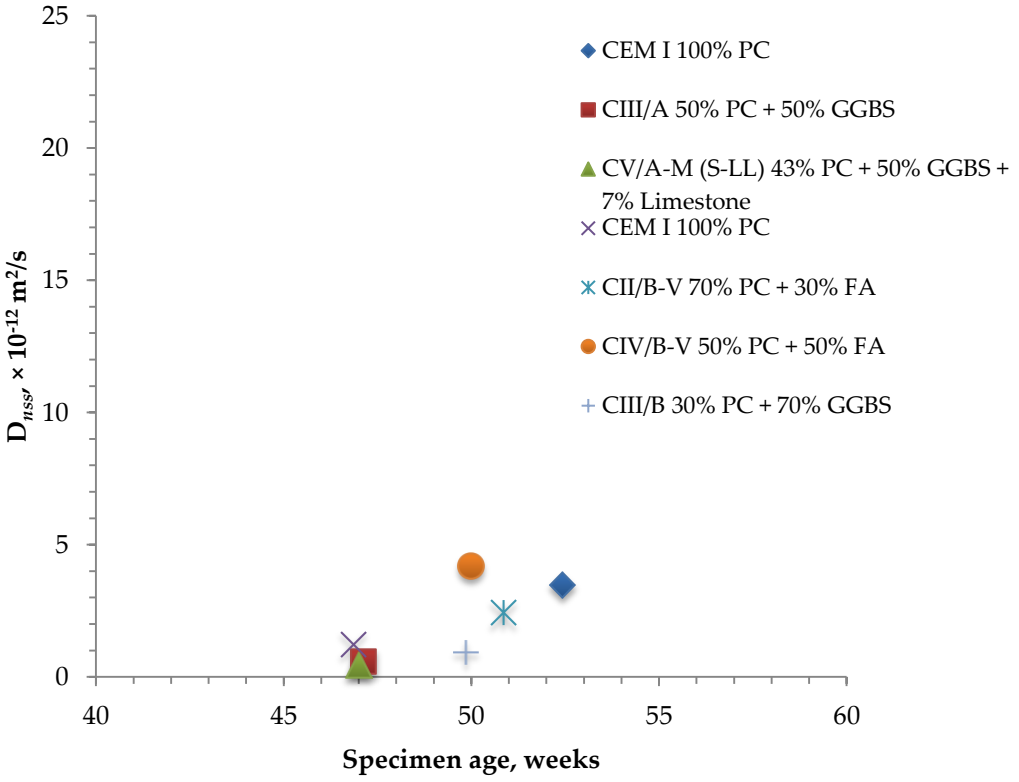


Figure 8.8 **Result of tidal cycle exposure**

8.4 RESULTS FROM THE INVESTIGATIONS OF THE RESEARCH GROUP

8.4.1 Performance of Concrete in Chloride Environments: Comparison of Performance Test Methods

There is an obvious difference when comparing compressive strength result from the different aggregate materials used in the main study. The average difference is almost 40% more with the Magnesian limestone compared to the gravel aggregate. Most affected by the strength improvements are the 0.40, 0.50 and 0.55 water-cement ratio CIV/B-V, 0.45 and 0.50 water-cement ratio CIII/A and 0.50 water-cement ratio CIII/B, with 27.5 N/mm^2 average increase in compressive strength with the Magnesian limestone aggregate.

It was found that even with a decrease in solution volume in the inversion test from the specified 12.5 ml/cm^2 area to about 4 ml/cm^2 area, D_{nss} compared between all 3 tests does not significantly differ. Figure 8.9 shows the comparison of D_{nss} values measured with ponding, immersion and inversion procedure. However, C_s value was found to be lowest in the inversion test compared to the ponding and immersion tests although only on average decrease of 26%, not in proportion with the decrease in solution volume which is 68%. It seems that even though the decrease on solution volume decreases C_s, the measurement of D_{nss} is not affected.

8.4.2 Effects of Ageing and Leaching on Rapid Chloride Migration Test

Storing concrete specimens in deionised water causes leaching of portlandite ($Ca(OH)^2$). The result shows that the 5 mm surface had an average of 27% reduction of portlandite content compared to the centre of the surface for CEM I at 28 days leaching. This figure then increased to 37% reduction from centre to the surface when leached for 56 days. CIII/B concrete reduced by 55% average at 56 days from 23% reduction at 28 days. Leaching increases with increasing water-cement ratio. For example, CII/B-V concrete with water-cement ratio of 0.35, 0.45, and 0.55 had a loss of portlandite of 3%, 18% and 37% at 28 days leaching respectively. Limestone mix had the lowest Portlandite reduction among all concrete mixes. Figure 8.10 shows the comparison of Portlandite loss for all concrete mixes from 28 and 56 days.

The effect of Portlandite loss on PD index measurement can be seen in Figure 8.11. The PD index measurement prior to leaching at 28 days and 90 days shows a decrease of the index for all tests. The PD index post-leaching measured at 118 days (28 days leaching) and 146 days (56 days leaching), records increase in the index. This increase in tandem with the loss of

portlandite due to the effect of leaching leaving the specimens more porous, thus lowers their resistance to chloride ingress.

The study found that CEM I concrete is the most vulnerable to leaching whilst fly ash and ggbs are less affected. It was reasoned that the pozzolanic and latent hydraulic reactions in these materials contributed towards Portlandite consumption as well as densifying the microstructure of concrete.

8.4.3 Effect of Brucite on Chloride Ingress

Concrete powder sample ground from the surface of the specimen was tested for Brucite using XRD. The results showed that Brucite peaks were insignificant. Because of that, its quantity was unable to be determined. Figure 8.12 shows the typical plot of surface powder sample and the location of Brucite peak in relation to the corundum marker. The diffusion coefficient D_{nss} was recalculated by the author. It was found that the calculated surface chloride content (C_s) is generally higher with specimens exposed to 1 M $MgCl_2$ by an average of 23%. However, D_{nss} values are higher with 2 M NaCl although the increase is not particularly significant, the most by 1.74×10^{-12} m^2/s.

The problem with trying to measure Brucite content with the XRD was partly as a result of the sampling procedure as the literature reviews pointed out that the thickness of the Brucite layer is limited to about 35 μm. The sampling procedure for the surface of the specimen is 1 mm grinding depth that produces between 1 to 3 grams of powder. Inadvertently the sample will consist of a high ratio of paste and aggregate materials to Brucite. Even though the concentration of $MgCl_2$ used is 10 times higher than that of natural seawater the result shows inconclusive evidence of Brucite.

There is a general increase in D_{nss} value with pure NaCl (average 30%) exposure compared to $MgCl_2$. However, to conclude that this is due to the pore blocking effect is premature. Figure 8.13 shows that the reason for the low D_{nss} value for $MgCl_2$ exposure is due to the different chloride profile although the depth of penetration is the same. The profile shows that $MgCl_2$ exposure has higher C_s value and this has an effect of lowering the D_{nss}.

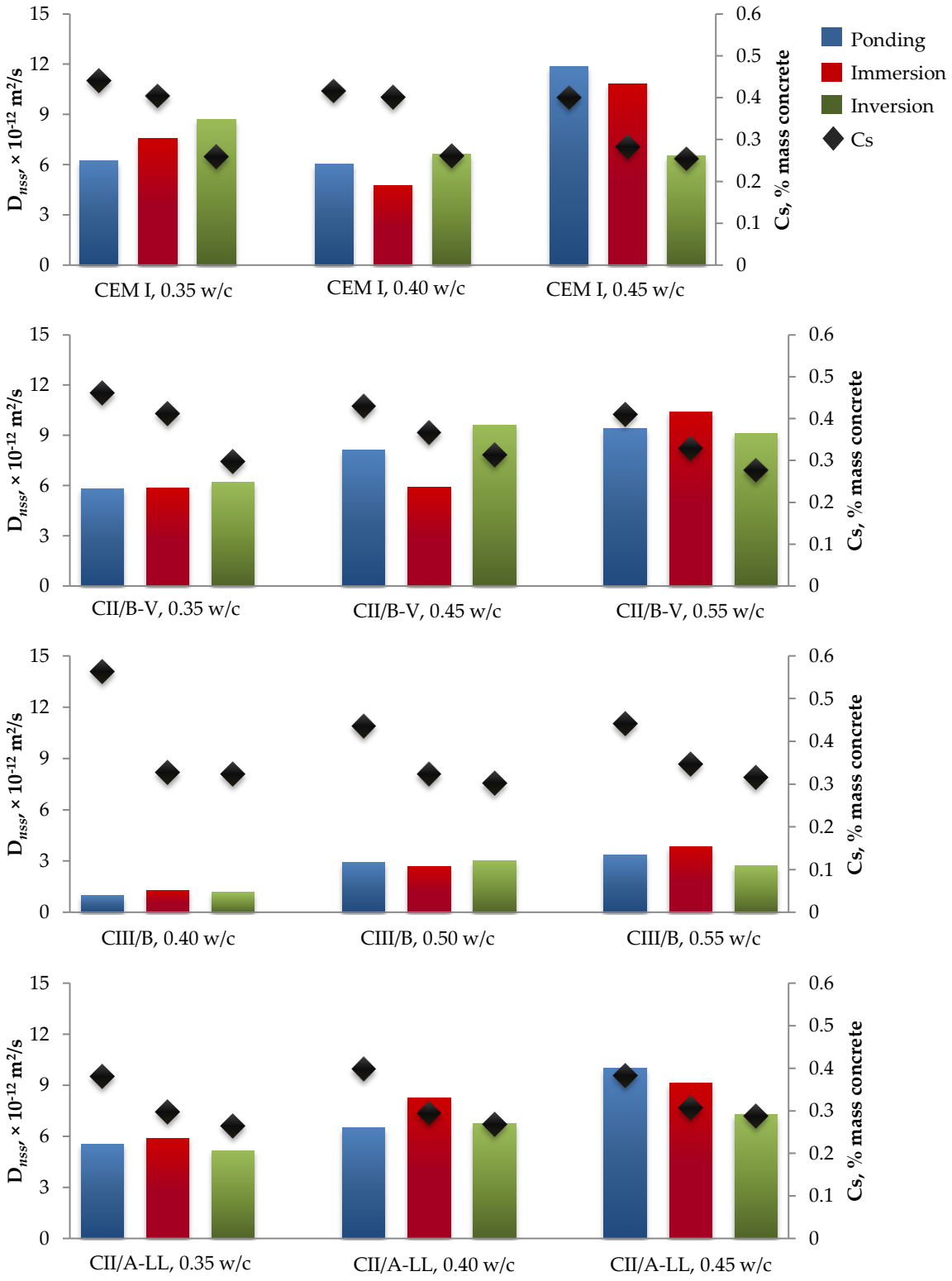


Figure 8.9 **D_{nss} value comparison between ponding, immersion, inversion and the associated surface chloride values.**

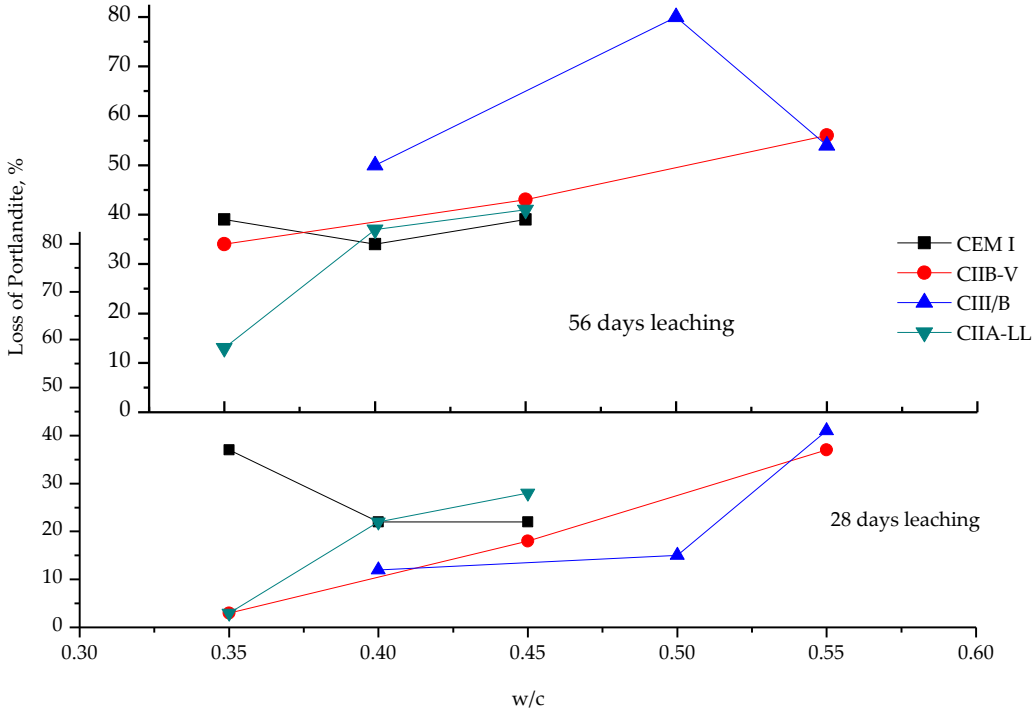


Figure 8.10 Comparison of portlandite loss from 28 days to 56 days

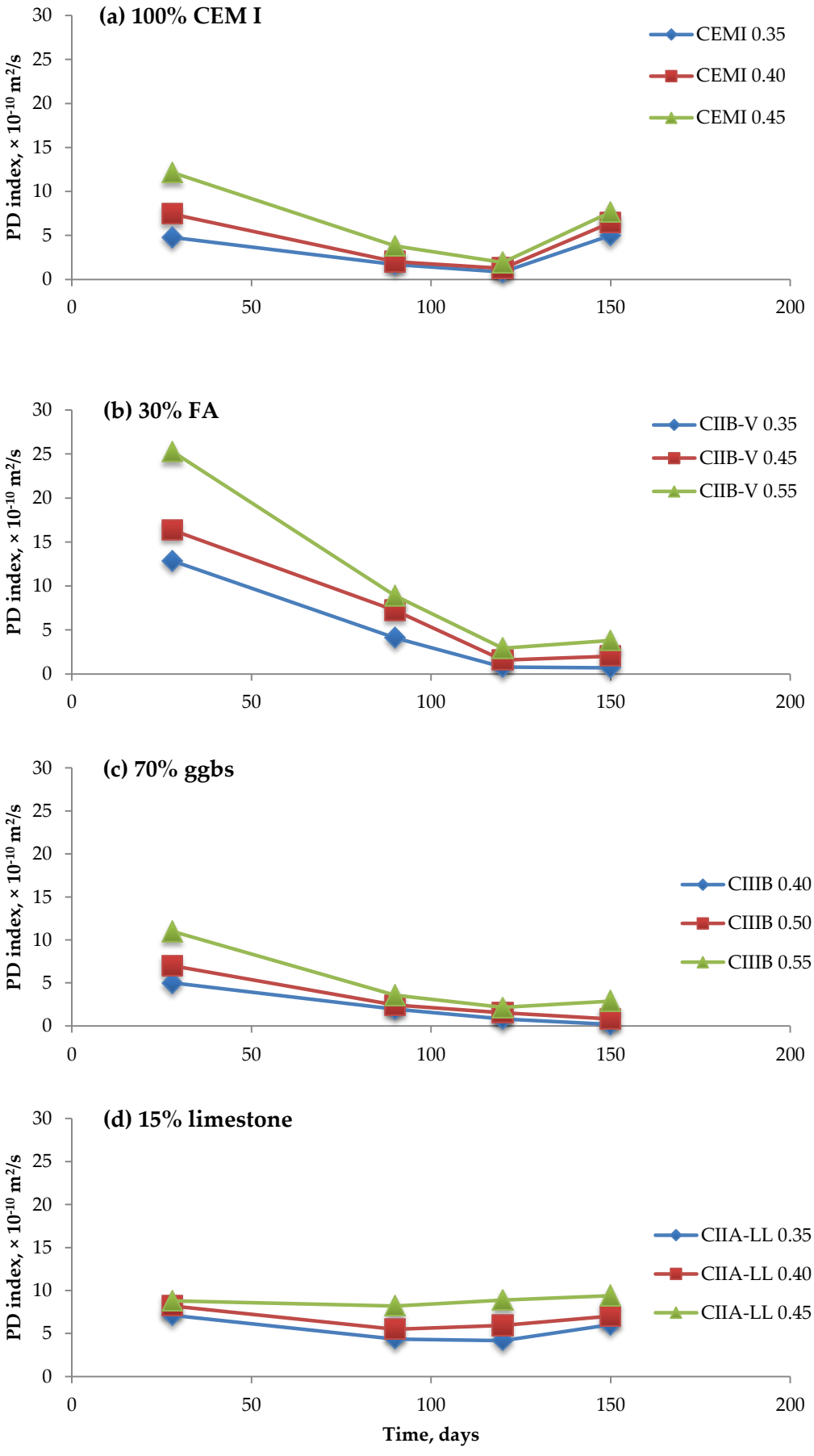


Figure 8.11 Effect of storage time in deionised water on the PD index

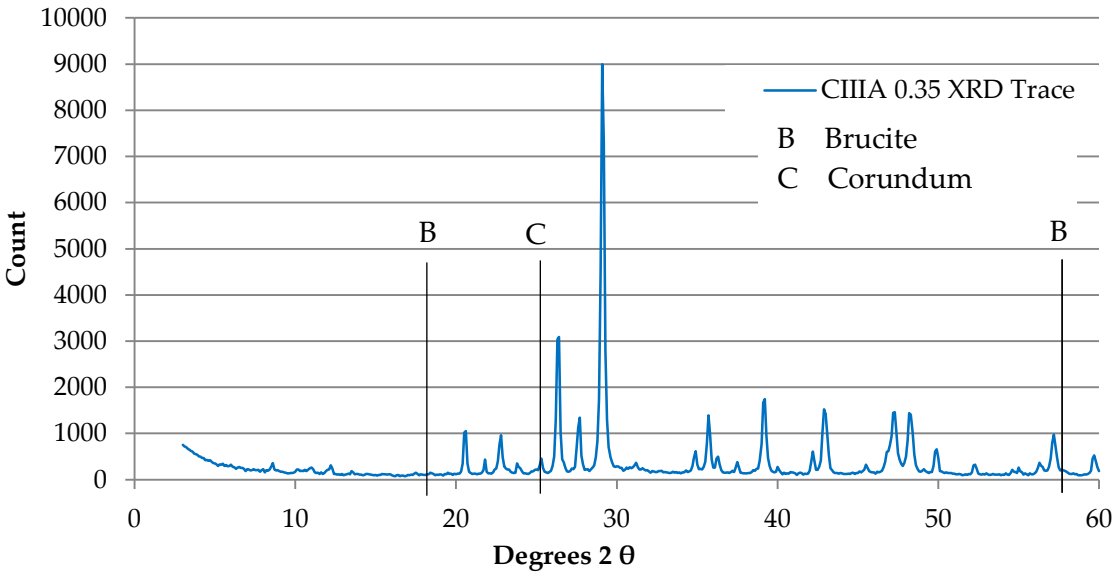


Figure 8.12 Typical XRD plot of concrete surface powder sample

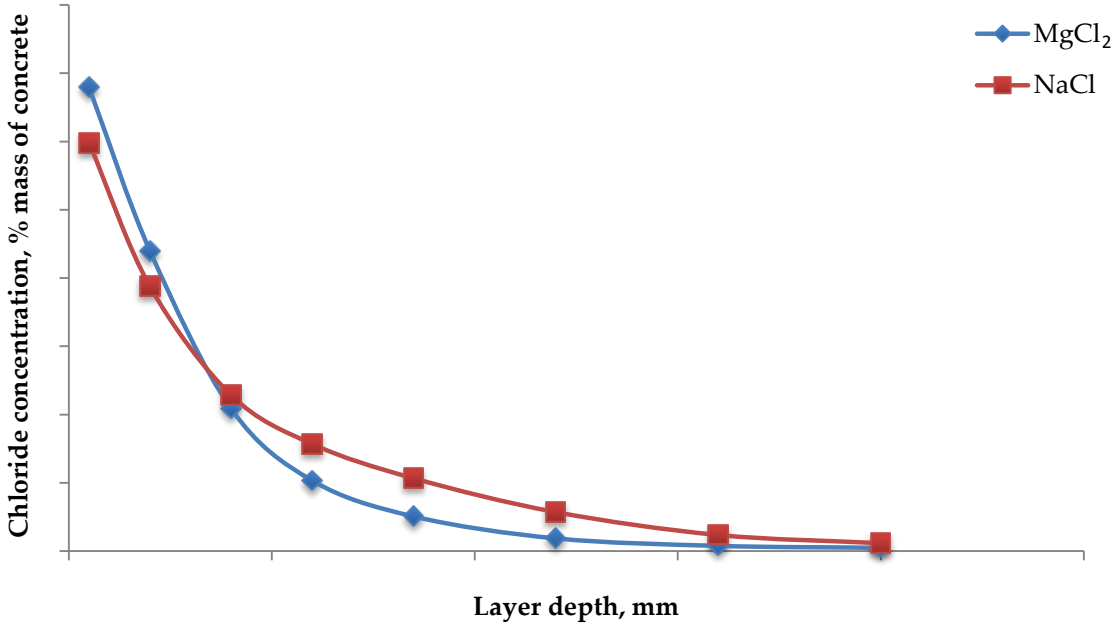


Figure 8.13 Typical chloride profile for $MgCl_2$ and NaCl

CHAPTER 9. DISCUSSIONS

9.1 CONCRETE AT THE LIMIT STATE OF BS 8500-1:2006

Concretes at the limiting values recommended in BS8500-1:2006 have a wide range of chloride diffusion coefficients whether it is measured with CEN TS 12390-11:2010, NT Build 492 or Multi-regime test. As a whole, all concrete at the limiting values of BS8500-1:2006 falls between 20×10^{-12} m^2/s to 0.3×10^{-12} m^2/s for all tests. This wide range of results shows that some of the mixes recommended in the standard for XD3 and XS3 exposure have high diffusion coefficients and may not last to the intended working life in chloride exposure environment.

There are mixes recommended in the standard that are likely to end with lower strength than the characteristic strength. These were recognised early during the thesis mix design stage and it was shown in a separate study that strength can be improved by the choice of aggregate and cement. It is therefore acknowledged that the choice of gravel aggregates used in this thesis, contributed to the overall performance of the concrete tested.

9.1.1 Effect of cement type

9.1.1.1 CEM I and limestone binary combination

CEM I and CII/A-LL mixes are generally at the ceiling of the scale for all tests when compared at either an equal strength or equal water-cement ratio. It was also observed that the concrete profiles of these 2 mixes are linear signalling the low level of chloride binding. Profiles of fly ash and ggbs concrete which are known to bind chlorides either as Friedel's salt or within the C-S-H gel are non-linear (exponential decay) suggesting the occurrence of chloride binding.

During the early age, the diffusion coefficient performance of 0.40 and 0.35 water-cement ratio CII/A-LL mixes are shown to be almost similar to the CEM I mixes at the same water-cement ratio across all the test methods. In some cases they perform almost similar to the fly ash mixes although being in the second group, fly ash mixes are at a higher water-cement ratio. However, the characteristic strength for the first and the second group and the resulting compressive strength differs by at least 15 N/mm^2. This means, even if the diffusion coefficient performance of the first and the second group may be the same, the compressive strength i.e. the mechanical properties of the concrete is different.

As the performance may be achieved from using type II additions at sometimes higher water-cement ratio, it shows water-cement ratio alone is not sufficient as an indicator for durability as binding potential inherent in different cement types has to be taken into account.

9.1.1.2 Fly ash

Fly ash mixes generally shows poor performance in the early ages of the test but found to be the most improved compared with other mixes. The overall ageing exponent of fly ash mixes are the highest (-0.774) compared to other mixes. It was observed that due to the high water-cement ratio limit recommended by the standard, the compressive strength of the fly ash mixes at 28 days are low by as far as around half of the target strength in the case of CIV/B-V (50% fly ash) mixes. These CIV/B-V mixes only attains 12 N/mm^2 for the 0.55 water-cement ratio and 16 N/mm^2 for the 0.50 water-cement ratio to a target of 30 N/mm$_2$. The low compressive strength in turn affected their diffusion coefficient when compared on the basis of w/c ratio only and not the full set of recommendation given in BS8500.

The choice of aggregate material is equally important to achieve minimum recommendation of the standard. In the study by the research group described in Section 3.6.8, it was found that a 50% fly ash with a 0.55 water-cement ratio using harder aggregate (magnesian limestone) 28 day cube strength is 26 N/mm^2 which is closer to the characteristic strength of 30 N/mm^2 compared to only 12 N/mm^2 attained with natural gravel. In this respect, the minimum strength is a good way in which the quality of the aggregate may be controlled in BS 8500-1:2006 standard.

The difference in fly ash level has shown that at the 20 weeks reference age, the performance of the 30% fly ash mix is marginally better than the 50% fly ash mix for both 40 N/mm^2 and 50 N/mm^2 equal compressive strength. It is known that the amount of aluminate content affects chloride binding (Thomas et al., 2012). The difference of Al_2O_3 content between both mixes is 3.2% where the content in the 50% and 30% fly ash mix is 12.1% and 8.9% respectively. However, counter intuitively, at both equal strengths the water-cement ratio of the 30% fly ash mix is higher in both instances. This pattern is consistent for CEN TS 12390-11:2010 and multi-regime, except it is reversed with the NT Build 492 test. Although the difference is within the error of the test, it shows that there is not much difference between increased replacement levels for the mixes studied.

Part of the problem with the fly ash mixes may come from the quality of the fly ash after the switch to the low NOx/SOx burner having 10% less strength activity index, low pozzolanic activity (Fox and Constantiner, 2007) and coarser than CEM I although it still conforms to EN 450-1 standard for category S fly ash.

9.1.1.3 Blastfurnace slag

Ggbs mixes are the best performing in all the tests. They generally returned lower D value in the early stage of the test and continued to improve although at a more modest rate than the fly ash mixes. However, ggbs mixes are never above 5×10^{-12} m²/s at any stage of the test and this is consistent for all test methods. The result also shows that the higher the replacement level, the better the performance of ggbs concrete. Even at a similar replacement level of 50% compared with fly ash, ggbs mix is better (11.5×10^{-12} m²/s vs. 4.6×10^{-12} m²/s for CEN TS 12390-11:2010 at 20 weeks) due to the higher compressive strength attained by the ggbs mix (16 N/mm² vs. 25 N/mm² at 28 days with similar strength at 1 year of 43 N/mm²).

With regards to aluminate content, ggbs mixes ranges between 8.2% to 9.8% of total cement, which is slightly less than the aluminate content in fly ash mixes regardless of the higher replacement percentage of the ggbs mixes. However, the silicate to aluminate ratio is higher in ggbs compared to fly ash (2.9 vs. 2.1). Some academics reasoned that low silicate to aluminate ratio may retard the formation of calcium silicate hydrate and make the concrete more porous. Despite the higher binding potential, due to the porosity of the fly ash mixes, diffusion is faster compared to ggbs.

The ageing exponent exercise shows that modern ggbs has a low initial diffusion coefficient compared to the ones used in for the calculation of ageing exponent reported in the Concrete Society Technical Report 61. An investigation into the sources of data for the ageing exponent of that report showed that the prevailing exponential slope was heavily influenced by data from the late 1980's. As more data from recent studies are available, maybe it is time that the ageing factors are revisited to reflect current conditions.

9.1.1.4 Ternary blends

The best all round performance in all the test method is a ternary blend concrete comprising 46% CEM I, 46% ggbs and 8% silica fume (CV/A-M (S-LL)). Ternary blend comprising ggbs and silica fume has also been reported performing consistently high in other tests (Bleszynski et al., 2002, Elahi et al., 2010). The other ternary blends show better performance compared to their closest equivalent in terms of equal strength and equal water-cement ratio. For example, mix D8 and D2 (CV/A-M (V-LL) and CII/B-V) both had equal water-cement ratio of 0.50 and compressive strength of 31.5 N/mm² and 31 N/mm² respectively but the D_{nss} value for the ternary blend is 5.0×10^{-12} m²/s better for CEN TS 12390-11:2010 and 11×10^{-12} m²/s for NT Build 492. This is achieved only by the replacement of 10% cement with limestone. However, the D_{ss} value for multi-regime 1.2×10^{-12} m²/s is better in favour of the binary CII/B-V mix.

9.1.1.5 Cement groups in BS 8500-1:2006 with respect to durability performance

The grouping of cements in BS 8500-1:2006 is supposed to be based on durability recommendation with an intended working life of either 50 or 100 years. Results of the study suggest that the groupings of cement/combination types are not reflective of the expected durability performance. As an example, in the first group, IIA represents a broad class of addition based on EN 197-1. Consequently the diffusion coefficient performance is similarly broad, in this thesis ranging from 2×10^{-12} m^2/s to more than 25×10^{-12} m^2/s. The research also suggests that CEM I concrete should not have been considered if long term durability is intended in the first place.

Cement groups may be best represented by cement types because chloride binding capacity seems to be the overriding factor. In this regard, taking water-cement ratio of 0.45 as the reference, CIII/A, CIII/B and CII/A-D are in one group whilst CII/B-V, CIV/B-V and composite cements containing at least one element from the first group are in the second group. These 2 groups should be adequate for durability.

9.1.2 Effect of water-cement ratio

The effect of lowering water-cement ratio to the diffusion coefficient is clear. At all ages and all cement types, lower water-cement ratio gives lower diffusion coefficient value across all test method. However, it was also found that there is a limit to the improvement of D value with the reduction of water-cement ratio. This can be seen especially when using cements that provides good resistance to chloride ingress such as ggbs. As the diffusion coefficient obtained with this mix is low to start with, there is hardly any change in D value for all test methods going from 0.45 water-cement ratio to 0.41 water-cement ratio for CIII/A and 0.45 water-cement ratio to 0.37 water-cement ratio for CIII/B.

9.1.3 Effect of age of test

The age, according to the test specification refers to the age of the specimen when it is exposed to the chloride exposure. The result of the thesis shows that as age of test increases, measured diffusion coefficient decreases with all test methods and at all water-cement ratio. The rate of the decrease in D is highest with fly ash concretes. This is because their 28 days compressive strength is lowest amongst all mixes tested causing a high initial D value. Subsequent pozzolanic reaction provides improvement in compressive strength and its high aluminate content binds chloride ion bringing a reduction in D value.

The reduction of D with age shows an exponential decay effect and this is more pronounced for concrete with diffusion coefficient value of more than 5×10^{-12} m^2/s. Concrete hydration may continue up until 20 – 30 years until all the available water in the system react with un-hydrated particle although the strength gain stabilises after about a year. In theory at least, the effects of ageing will continue throughout the same period as hydration.

9.1.4 Effect of exposure period

The study into the effect of exposure period to chloride diffusion shows that with respect to the CEN TS 12390-11:2010 test method, 90 days exposure is the optimum test period. The results shows that at the specified minimum volume of 12.5 ml/cm^2 surface area of the specimen, the rate of diffusion stabilises after 90 days and the D_{nss} value measured did not change significantly afterwards.

However, the study brought forward the question of comparing the CEN TS12390-11 test with the NT Build 443 test that has a shorter exposure period of 35 days and a higher chloride concentration (10% NaCl). It is based on the author's understanding that the likely performance of the CEN TS 12390-11:2010 was derived on the observation from NT Build 443 test method. The stability of the rate of diffusion from the short exposure condition based on NT Build 443 needs to be verified.

9.1.5 Effects of artificial seawater exposure

Exposure of concrete specimens to artificial seawater in a tidal tank for cyclic wetting and drying procedure shows that in general, chloride ingress process is different in seawater compared to NaCl exposure. Despite limited success in precipitating brucite ($Mg(OH)_2$) on the surface of concrete, diffusion of chloride in artificial seawater in a cyclic condition is lower by 50% to 90% in 5 out of 7 specimens tested compared to the fully submerged tests. However, the results of the study by the research group, which used a $MgCl_2$ and NaCl cyclic exposure, and was different to that of the main work described in the thesis, shows that there was no difference.

Although brucite was sometimes cited as beneficial skin that may protect concrete from chloride ingress, it was found that in studies conducted on concrete specimen, the contribution of brucite in chloride resistance was largely inferred based on the spectrographic identification of brucite on the surface of the specimen. This phenomenon is then referred to in a study by Buenfeld, (1986) on mortar specimens that show the development of brucite and aragonite layers on the surface and are linked to reduced permeability and resistivity of concrete.

From the result of the study, and the lack of conclusive determination of brucite despite the reduction in D, the author believes that brucite plays no significant part in resisting chloride ingress. There is another plausible explanation that discusses the role of sulfate in seawater which competes with chloride for binding sites particularly with C_3A. The presence of sulfate ion in pore water is shown to negatively impact physical and chemical binding of chloride (Zibara, 2001). Diffusivity of sulfate ion through Portland cement-based systems is ≈ 100% slower than chloride ion (2-30 × 10^{-14} m^2/s) (Lea and Hewlett, 1998) and as diffusion pathways is chocked, chloride diffusion slows down. However, sulphate ion content at and near the surface zone was not measured as part of the experimental programme and this remains as a hypothesis.

9.2 DISCUSSION ON THE CEN TS 12390-11:2010

9.2.1 3 methods of exposure

The Technical standard currently allows for 3 different exposure methods i.e. immersion, ponding and inversion. This may be considered unnecessary as there is the risk that they may produce different result. The effects of the different exposure method were studied in one of the research group project. It was found that the different exposure method did not produce a different D although C_s was low on the inversion method compared to ponding and immersion. At the recent round-robin conducted by CEN, different exposure regime is also investigated. The result of the round-robin exercise is being finalised by IETcc at the time of writing this thesis.

From experience, the ponding version of the test is relatively hardest to get right. The ponded specimens have a slightly different preconditioning process where after vacuum saturation the surface needed to be patted dry and the surface prepped up to receive the pond. Sealing the pond on top of the specimen often time requires the surface to be dried sufficiently (at least 'white-dry') so that sealant for the pond can attach and cure properly. Curing the sealant may take additional 12 hours up to 24 hours of further drying depending on the compound used.

As the specimen has been vacuum saturated, leaving it to dry for that period of time seems counter-productive. Then, as the test progressed, ponds are rarely leak free. This is because over time as the exposure solution seeps under the sealant and concrete surface, the bond between them weakens. As a result, leakage is a common occurrence and the solution has to be regularly topped up to the required minimum volume of 12.5 ml per cm^2 exposed surface as stated in the test methodology. What this does to the test precision is not entirely known.

The immersion and inversion version are usually easy to perform and requires minimal handling. After coating with epoxy or wax, they are put into saturated CaOH solution for 18 hours and then transferred straight into the exposure solution without any other treatment. The test prescribed a minimum volume of 12.5 ml per every cm^2 of exposed surface and there are studies that show having a variable volume have an effect on the chloride profile characteristics. It is not known whether having too much solution can affect the profile characteristics. Standardisation of a single exposure is preferable to minimise variation.

9.2.2 Use of profile grinding to obtain concrete sample

Profile grinding is a time consuming process. Using a handheld profile grinder with a diamond bit tip requires at least 40 minutes per 8 layers sample. Due to the vibration and the dust generated, health and safety requirements have to be adhered to regarding prolonged working in these conditions.

The amount of time required to do the profile grinding is taken up mostly to achieve the accuracy with regards to depth of each of the layers as the first few layers of some concrete type needed to be ground at 1 mm intervals. For the purpose of this thesis, the accuracy level is ±0.3 mm. A better way is to use a mechanised lathe and a milling machine to collect the sample concrete dust. This may shortened the time required to do the work with higher accuracy and better control in terms of health and safety.

9.3 BEST FIT OR THEORETICAL CURVE PROFILE

The calculated diffusion coefficient is dependent on C_s value. However, the research community has yet to agree the method of arriving at the value (Jones, 2011). As there remains to be consensus, the C_s value for this thesis is determined automatically using a regression analysis script proposed by Tang Luping of Chalmers Insitute and cross checked using Matlab script developed by Christopher Thistletwaithe. It was found that the C_s value obtained by both scripts were almost identical. The difference is ±2% or second decimal places which may be regarded as insignificant.

In cases where the best fit curve starts not from the second data point but at later data points, the earlier data points are discarded to enable fitting to the best fit. This increases the C_s value but lowers the diffusion coefficient as the regression slope becomes steeper and the data points fits better. In this case it can be argued that the C_s value extrapolated from the regression back to zero

is not the true surface chloride concentration but the value derived to obtain a good fit to the regression analysis.

Another method was proposed by Andrade (2002) involves rescaling the regression curve to the maximum measured concentration. However, the author did not go down this route as the diffusion coefficient obtained is the apparent point-wise diffusion, (i.e. averaged diffusion value at the time of testing) and thus time dependant whereas the rescaling procedure proposed suggested that the time is irrelevant. Figure 9.1 shows the proposed rescaling procedure (Andrade, 2002).

The phenomenon where the best fit curve is away from the second data point is often observed in long term field exposure concrete and termed 'convection zone' (Lindvall et al., 2000, Nanukuttan et al., 2008, Tang et al., 2012). However, it is also observed in this thesis occurring in laboratory specimens as shown in Figure 9.2. In this respect the author proposed the zone where the chloride concentration seems to be constant at several chloride profile depth to be called the saturation zone.

The surface zone in laboratory specimens may contain microstructural cracks as artefacts from diamond sawing to expose the bulk concrete according to the test procedures. It is expected that this layer to have variable chloride concentration. That is one of the reasons why the first millimetre layer is always discarded in the regression analysis. The surface zone is also where ion exchange occurs by the interaction of mobile ionic liquids of the concrete, i.e. sodium, potassium and hydroxyl ions, together with the diffusion of chloride ions (Tang et al., 2012).

After the surface layer, is where sometimes the saturation zone may develop. Convection can be ruled out as the specimens were not exposed to the elements. A possible explanation for this happening in laboratory specimens is the gradual saturation of chloride ion within the pore fluids. During the early stages of the test, chloride ingress proceeds as diffusion due to concentration gradient as described in the classical literature explaining diffusion of chloride ion into concrete. As pore liquid becomes increasingly saturated with chloride ion, the upward increase of chloride content within the saturation zone slows down. Figure 9.3 shows the conceptual interpretation of the stages of the development of the saturation zone in the chloride profile.

The degree to which chloride is saturated depends on the rate of diffusion in the diffusion zone, the chloride binding capacity in the saturation zone and the chloride concentration of the exposure solution. In effect, the saturation zone may signal that chloride binding up to this zone has completed and the chloride is diffusing in this zone at a constant rate i.e. steady state. This phenomenon is easily seen in low strength, high water-cement ratio concrete at an early age. This

is because their interconnected porosity is higher compared to higher strength, low water-cement ratio concrete enabling faster diffusion. However, given enough exposure time it is envisaged that most if not all concrete may show the same effect.

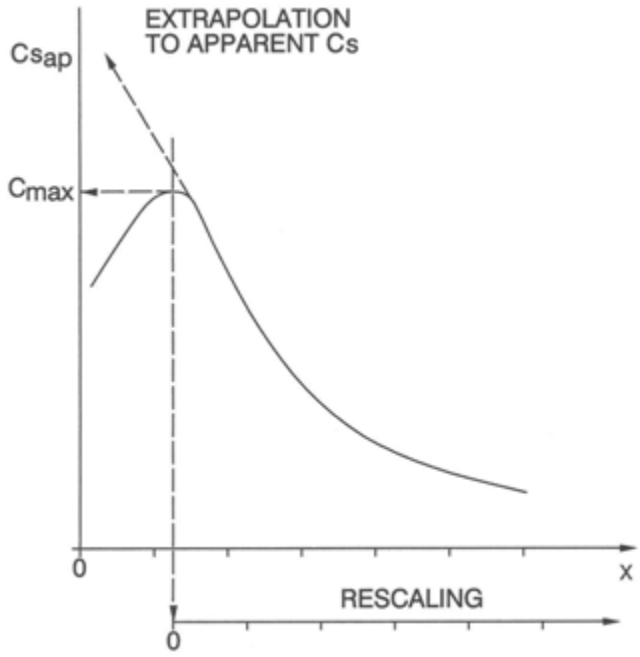


Figure 9.1 **Rescaling procedure proposed for obtaining D_{nss} (Andrade, 2002)**

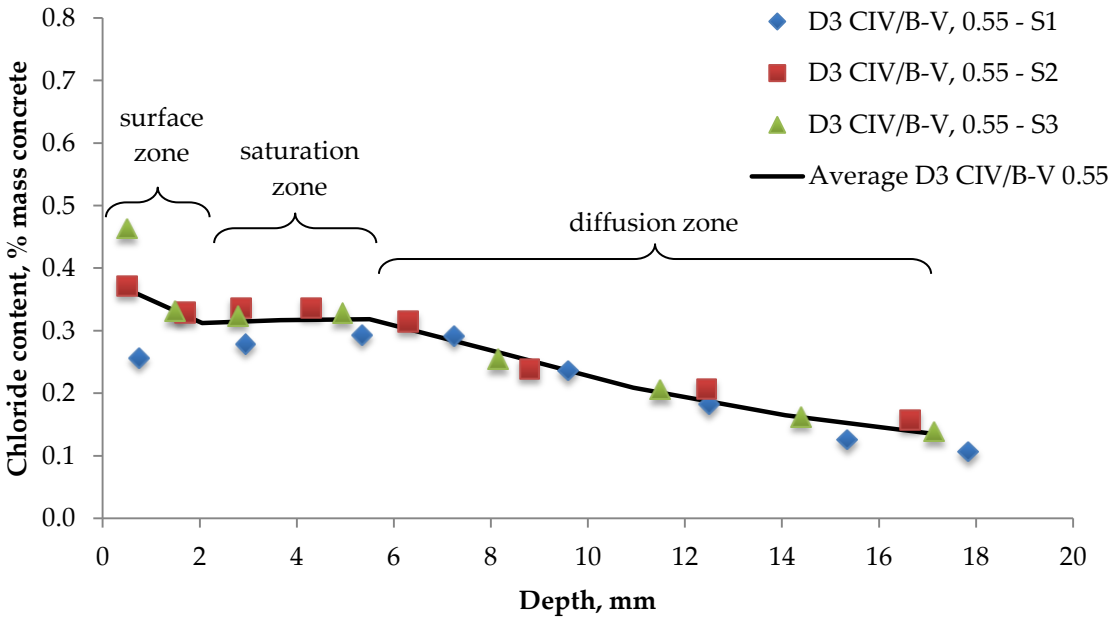


Figure 9.2 **Chloride profile showing a saturated zone, 90 days exposure, 9 weeks age**

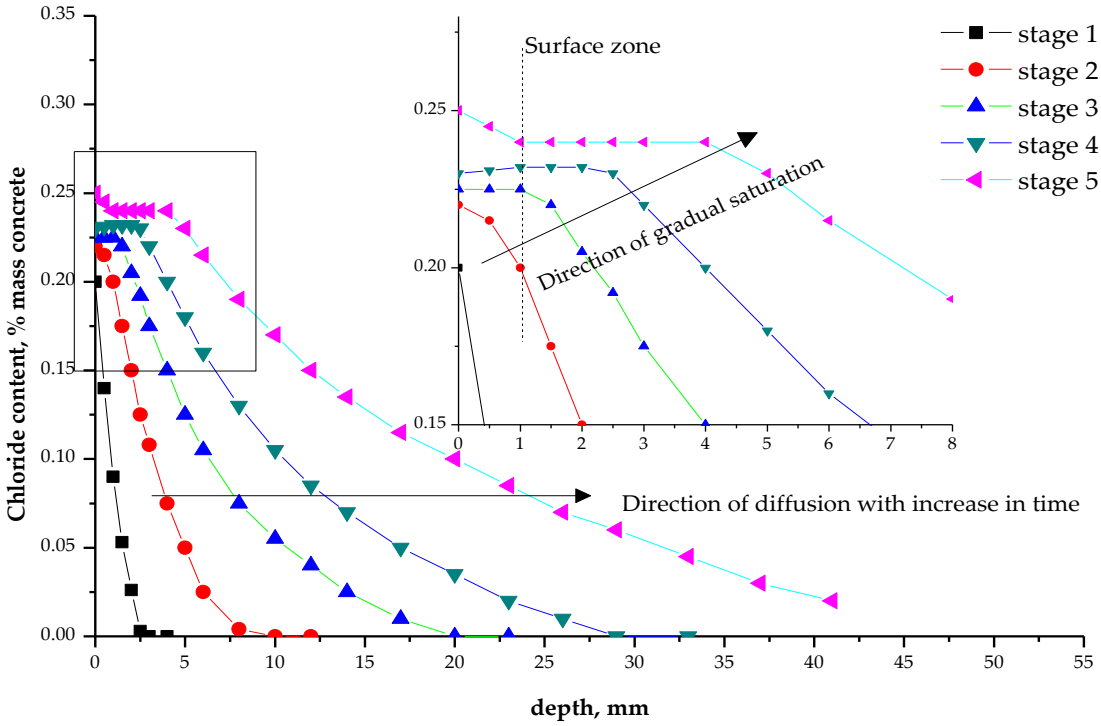


Figure 9.3 Hypothetical view of the development of saturation zone in the chloride profile

***Stage 1**; Start of chloride diffusion. **Stage 2**; Diffusion progresses, variability in the surface zone becomes visible. **Stage 3**; Chloride ions diffuses beyond the surface zone where ion exchanges occurs. **Stage 4**; Chloride ion started to saturate as all binding sites being exploited while diffusion front progressed. **Stage 5**; Saturation slows down the increase of chloride concentration within the specimen, binding in the saturation zone completed, diffusion front progresses further.*

9.4 COMPARISON BASED ON EQUIVALENT PERFORMANCE

The author is being given the impression that the direction of several of the European countries like the Nordic regions, Spain, Netherlands and Germany is to specify for durability in chloride environment based on water-cement ratio with minimum cement only. The prevalent UK practice is to specify durability based on water-cement ratio, minimum cement and compressive strength. Prime example is the EN 206-1 document, where in clause 5.2.5.3 specifically allows changes to the water-cement ratio and minimum cement with regards to equivalent concrete performance. A review of European research literature also shows that when it comes to durability, compressive strength was almost never mentioned. In this case, it can be implied that the importance of compressive strength is only for mechanical properties and it will be achieved in conjunction with the water-cement ratio.

With the use of Type II additions like fly ash and ggbs, the relationship of water-cement ratio and strength is different with different cements. For example, at 0.45 water-cement ratio, the range of strength between all the mixes studied for this thesis (with a single aggregate type) varies between 22 N/mm^2 to 53.5 N/mm^2. Given the difference, it does not necessarily means that the higher strength concrete will give better performance.

Table 9.1 shows the detail breakdown of the normalised compressive strength values for equivalent water-cement ratio of 0.45 and the normalised water-cement ratio values for the equivalent strength of 40 N/mm^2 and 50 N/mm^2.

At the equivalent water-cement ratio of 0.45, the 30 N/mm^2 (140%) difference in compressive strength translate to the difference in D_{nss} value for the CEN 12390-11 test method of 1.8×10^{-12} m^2/s to 18×10^{-12} m^2/s excluding CEM I mix that goes over the limit of 25×10^{-12} m^2/s, a 900% difference. Detailed normalised D value for each test methods can be referred to in Chapters 4-6.

Although water-cement ratio influences porosity and strength, for durability it has been argued the interconnectivity of the pore spaces is more important (Baroghel-Bouny et al., 2002b, Collepardi, 2005, Newlands et al., 2008). With sub-Portland size particles, a wide particle size distribution gives better particle packing and it can be speculated that this shifts the pore size distribution towards the micropores, constricting pathways from diffusing chloride ions even when total porosity may be similar between different mixes of a same water-cement ratio.

Furthermore, binding potential needed to be accounted for as in the case of ggbs cements where its resistance to chloride ion can be argued as far higher than is expected within the interconnectivity of the pore space. The current hypothesis is that it is due to the presence of thiosulfate ion that is

uniquely found the ggbs cements although this theory is not popular and so far has not been validated.

On the basis of the preceding arguments, the water-cement ratio alone is not the main driver, and equal performance with respect to compressive strength and binding potential i.e. cement types needs to be considered for durability.

Table 9.1 Normalised compressive strength and water-cement ratio based on 28 days compressive strength results for normalised mixes.

Normalised Mix Code	EN 197-1 Notation	Proportions	0.45 w/c	40 N/mm^2	50 N/mm^2
N1	CEM I 52.5 R	100% PC	47.0[A]	0.51[B]	0.43[B]
N2	CII/B-V	70% PC + 30% FA	40.5	0.42	0.36
N3	CIV/B-V	50% PC + 50% FA	22.0	0.36	0.33
N4	CIII/A	50% PC + 50% GGBS	37.5	0.44	0.41
N5	CIII/B	30% PC + 70% GGBS	33.0	0.41	0.37
N6	CII/A-D	92% PC + 8% SF	53.5	0.56	0.48
N7	CII/A-LL	85% PC + 15% LS	50.0	0.54	0.45

Note: Reference mix = CIII/A

[A] compressive strength, N/mm^2, 28 days

[B] water-cement ratio

9.5 IS IT THE TEST METHOD OR IS IT THE CONCRETE?

All three test methods show as water-cement ratio drops, the improvement to D is decreasing exponentially. This may suggests there is a natural diminishing improvement of reducing water-cement ratio or the test methods are limited at low water-cement ratio.

It is the author's opinion that the diminishing improvement in D is caused by limits in the concrete materials used rather than the limitation of the test method. It is acknowledged that fines content and a wide range of particle distribution is important because it gives a closed structure. As chloride diffuse principally through the pore system, more cement means more routes for chloride, but at the same time using cement with high binding potential like fly ash and ggbs give more chloride binding. Work carried out by Thomas et al., (2012) also shows that reducing water-cement ratio may actually retard binding as chloride ions are unable to get to the binding sites.

The limiting of improvement to the diffusion coefficient values of concrete mixes may be explained through the limit of compressive strength improvement with reducing water-cement ratio. It is known that water-cement ratio reduction increases concrete strength but at some point below 0.40 water-cement ratio (0.38 according to Neville, 1995), the reduction no longer contributes to strength improvement where the voids ratio is no longer improving. Going on a lower water-cement ratio past this point may risk introducing autogenous shrinkage and cracking.

Before arriving at the theoretical water-cement ratio limit, the diffusion coefficient of concrete depends on both the porosity and the chloride binding potential. At the water-cement ratio limit however, chloride diffusion depended more upon the binding potential as the diffusion through porosity is now constant. The constant porosity in this case is the basic rate of diffusion for any given concrete.

If the improvement in D value is caused by the limitation of the test method, there should be a water-cement ratio threshold where the test method can no longer detect difference in the D value. So far this is not the case. There is no observable threshold water-cement ratio because it seems that this differs between different cement types.

9.6 LIMITATIONS

9.6.1 Concrete porosity

It is acknowledged that in order to better understand the differences between mixes in terms of the relationship between diffusion coefficient and compressive strength, a form of porosity measurement would have been beneficial. However, it is accepted that concrete pore systems are not wholly interconnected whilst porosity measurement methods such as nitrogen absorption and mercury intrusion porosimetry relies on the assumption that pores are interconnected.

Furthermore, the literature review conducted shows that there are unsolved questions on the methods used to measure porosity. Mercury intrusion porosimetry for example introduced perturbance to the specimens due to the preconditioning process of drying out samples. The test itself is limited due to the irregularity of the pore geometry in cement systems (Abell et al., 1999).

Practically, paste and mortar studies will need to be conducted to arrive at a sound estimation of the porosity of any concrete. This in turn requires further research time allocated to mixing and the actual study. Due to the limited time available the author deemed that it was not feasible within this project.

Indeed porosity measurement has not been tried in this thesis directly, neither it is inferred indirectly through methods such as resistivity or pore volume calculation. This is because the knowledge of total porosity does not contribute to the analysis of pore size distribution needed to infer interconnectivity of the pore system.

9.6.2 Variability of results

Given the non-homogenous nature of concrete, test result are often variable. The coefficient of variation for CEN TS 12390-11:2010, NT Build 492 and Multi-regime was calculated as 27%, 12% and 17% respectively. The exposure version used for the CEN TS 12390-11:2010 was immersion. The coefficient of variation for the ponding and inversion test is currently unknown.

As these tests are designed to be used as input in the service life model, care has to be taken to make sure that variation of the test is as small as possible. Small variation in diffusion coefficient may mean wide variation in numerical models especially the probabilistic prediction that reaches 100 years.

To put it in perspective, the numerical difference between 1×10^{-12} m^2/s and 2×10^{-12} m^2/s is 100% but whether this translates in a 100% increase in performance with respect to the service life

modelling is unclear. The ageing factor proposed by the Concrete Society Technical Report 61 shows how variable the prediction could be as the range between the lower and upper bound in the log-log confidence interval is an order of magnitude different.

9.7 CHLORIDE RESISTANCE ON A MACRO LEVEL

Although not covered in this thesis, one has to remember that the design of concrete mixes to combat the threat of chloride ingress also have be balanced with factors like risk of carbonation, freeze thaw and effect of mix design on the ability to pump the concrete, cohesiveness of the mix and the risk of cracking.

For example in carbonation, it is known that high replacement of ggbs (>50%) has low carbonation performance. Freeze thaw environment requires air entrainment. Lowering water-cement ratio to improve performance does have its limits. This also needs to be balanced with the difficulty of working with very low water-cement ratio mixes.

Additionally, in order to re-connect the thesis with the needs of the construction industry, the question of construction economics is never too far behind. In perspective, the UK still produces abundance of fly ash (≈ 10 million tonnes/year) but not much in terms of ggbs (≈ 2 million tonnes/year). The cost difference of £30-£120/tonne and availability makes fly ash much more attractive to producers. Other Type II additions like silica fume and metakaolin is even more expensive.

With the construction industry going down the route of performance specification, the most economical and cost effective mix that conforms to the required performance will likely to be the goal for concrete producers (Andrade et al., 2008). Verifying the real performance of these mixes will have to be anticipated by standard developers.

CHAPTER 10. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDIES

10.1 GENERAL SUMMARY

In this chapter, the general conclusion from the results of the tests are presented in response to the aims and objectives set out in the first chapter of the thesis. The literature review and the subsequent research work have provided an insight to the performance of concrete within the framework of a limiting value methodology as practised in the current BS 8500-1:2006 and BS EN 206-1:2000 standard.

The literature review has shown that Europe is trying to adopt a performance-based specification and therefore has an interest in a test method with respect to chloride resistance whether rapid migration or natural diffusion. The strategy adopted is to pursue a fundamental diffusion coefficient test methodology, with the intention of application into service life models and at the same time solution for equivalent durability performance.

The merit of this strategy has also caused its development to be slow. So far, only a non steady-state natural diffusion test (CEN TS 12390-11:2010) requiring 119 days minimum period has been agreed. A rapid test method, more suited for practical engineering design has still not been agreed upon.

The research work has also furthered the understanding of the CEN TS 12390-11:2010 test method, while at the same time identified several new questions that need to be answered in order to move the industry from a prescriptive-based methodology of concrete design to a performance-based methodology.

10.2 CONCLUSIONS

10.2.1 Laboratory study on ageing effects using CEN TS 12390-11:2010

A comprehensive laboratory study was carried out to test the CEN TS 12390-11:2010 on mixes conforming to the limit values of BS 8500-1:2006. The ageing effect of these mixes was investigated by periodically testing them over the period of one and a half years. With all concrete, especially fly ash, D_{nss} values reduced over time showing improvements in the concrete with age.

In addition to the CEN test method, the UNE 83987:2009 and NT Build 492 tests were also conducted to identify the differences / similarity in performance and ranking of concrete between them.

It was found that extending exposure period for CEN TS 12390-11:2010 from 90 days to 120 days yielded minor differences in the D_{nss} values measured, suggesting 90 days exposure is optimum. It was also found that cyclic wetting exposure with artificial seawater reduced D_{nss} values.

10.2.2 Benchmark of concrete at the limit values of BS 8500-1:2006 using CEN TS 12390-11:2010

Some concrete mixes recommended at the limiting values of BS 8500-1:2006, in its current state for 100 year intended service life may not actually achieve this level of performance. This can be seen where, CEM I and CII/A-LL mixes performed poorly and did not improve with age.

The research work compares the normalised performance of concrete based on the compressive strengths of 40 N/mm^2, 50 N/mm^2 and water-cement ratio of 0.45 at 2 different ages of 20 weeks and 50 weeks. Taking the 20 weeks CEN TS 12390-11:2010 normalised performance as a reference, the author found that the ranking changed when 50 weeks normalised performance is compared. However, the change in ranking does not necessarily change the order in which cement types are ranked. Table 10.1 shows the rank order of concrete for all test methods at 20 and 50 weeks.

Ggbs mixes are found to have the best performance irrespective of test methodology. Fly ash and silica fume followed with CEM I and limestone mixes last. The best overall performance was achieved using a ternary blend of CEM I, ggbs and silica fume at 0.40 water-cement ratio.

10.2.3 Comparative performance between CEN TS 12390-11:2010 and electro-migration test methods

One of the aim of this thesis is to explore the possibility of having a faster and more practical way to rank concrete performance. The performance and ageing exponent for CEN TS 12390-11:2010 is found to be different to the performance and ageing exponents measured using electrically driven migration test methods. This shows that the performance between different test methods are not well correlated. There is no uniform ranking between the test methods, showing that ranking performance is not feasible with a rapid test.

The comparative performance exercise however shows that with all test methods, the rate of improvement in the performance of concrete reduces with water-cement ratio.

Table 10.1 Ranking of concrete mixes for all test methods

Test method	Equivalent performance:	Ranking (best – worst)
20 weeks CEN TS 12390-11:2010	40 N/mm²	CIII/A> CIII/B> CII/B-V> CIV/B-V> CII/A-D
	50 N/mm²	CIII/A> CIII/B> CII/A-D> CII/B-V> CIV/B-V> CII/A-LL
	0.45 w/c	CIII/A> CIII/B> CII/A-D> CII/B-V> CIV/B-V> CII/A-LL
50 weeks CEN TS 12390-11:2010	40 N/mm²	CIII/B> CIII/A> CII/B-V> CIV/B-V> CII/A-D> CII/A-LL
	50 N/mm²	CIII/B> CIII/A> CII/A-D> CII/B-V> CIV/B-V> CII/A-LL
	0.45 w/c	CIII/B> CIII/A> CII/A-D> CII/B-V> CIV/B-V> CII/A-LL
20 weeks NT Build 492	40 N/mm²	CIII/B> CIII/A> CII/A-D> CIV/B-V>CII/B-V>
	50 N/mm²	CIII/B> CIII/A> CII/A-D> CIV/B-V>CII/B-V> CEM I> CII/A-LL
	0.45 w/c	CIII/B> CIII/A> CII/A-D> CIV/B-V>CII/B-V> CII/A-LL> CEM I
50 weeks NT Build 492	40 N/mm²	CIII/B> CIII/A> CIV/B-V> CII/B-V> CII/A-D>
	50 N/mm²	CIII/B> CIII/A> CIV/B-V> CII/B-V> CII/A-D> CEM I> CII/A-LL
	0.45 w/c	CIII/B> CIII/A> CIV/B-V> CII/A-D> CII/B-V> CII/A-LL> CEM I
20 weeks Multi-Regime	40 N/mm²	CIII/B> CII/B-V> CIII/A> CIV/B-V> CII/A-D> CEM I
	50 N/mm²	CIII/B> CII/B-V> CIII/A> CIV/B-V> CII/A-D> CEM I> CII/A-LL
	0.45 w/c	CIII/B> CIII/A> CII/B-V> CII/A-D> CIV/B-V> CEM I> CII/A-LL
50 weeks Multi-Regime	40 N/mm²	CIII/B> CIV/B-V> CII/B-V, CIII/A> CII/A-D> CEM I
	50 N/mm²	CIII/B> CIV/B-V> CII/B-V> CIII/A> CII/A-D> CEM I> CII/A-LL
	0.45 w/c	CIII/B> CIII/A> CII/B-V> CIV/B-V> CII/A-D> CEM I> CII/A-LL

10.2.4 Ageing factor for chloride resistance

This thesis has added to the validation of the ageing factor values proposed by Concrete Society Technical Report 61. It shows that CEM I, limestone, silica fume and fly ash cements have produced compatible performance with respect to the ageing factor. The data for ggbs shows that the ageing factor for ggbs may need to be updated to take into account the change of performance of current ggbs cements/combinations.

With respect to the test methods, the non-steady state tests, CEN TS 12390-11:2010 and NT Build 492 has good compatibility with the ageing factor. However, the exercise has also shown that the steady state migration test is not compatible with the ageing factor contained in the report.

10.2.5 Normalisation of test data

The normalisation procedure shows that the performance of concrete measured on an equal water-cement ratio basis may not be similar to the performance measured on an equal compressive strength basis. This underlines the need to take into account compressive strength together with water-cement ratio and minimum cement content in designing for chloride resistance using the limiting factor methodology.

In this respect, the European practice of concrete specification for durability based on water-cement ratio and minimum cement needed to be expanded to compressive strength. In the future as performance specification becomes established with a robust performance test methodology, the limiting values of the prescriptive standard can be dropped.

10.3 RECOMMENDATIONS FOR FUTURE WORKS

i. As the CEN TS 12390-11:2010 standard is still at its infancy, there remains a lot of testing work still to be done. The range of concrete tested in this thesis is limited to the mixes at the limit of the BS 8500-1:2006 standard. Further programme for the CEN TS 12390-11:2010 may include design mixes typical of real-world and current infrastructure projects in collaboration with the industry. Aggregate should be varied to investigate the difference in aggregate absorption rates to concrete performance. The effects of admixtures such as superplasticisers and water reducers should also be investigated. This may serve as input to improve upon the service life models.

ii. The CEN TS 12390-11:2010 only specifies a minimum volume of solution for the test. An experimental programme to explore the effect of exposure volume above the minimum requirement should be initiated to specify a ceiling volume for the test.

iii. The difference in D value measurement between pure NaCl and artificial seawater exposure justifies a test programme to explore further the effects of this phenomenon. It is suggested that a programme that compares static exposure of specimens in pure NaCl and artificial seawater in accordance to CEN TS 12390-11:2010 to be carried out. There is also a question of disconnect, between laboratory test in artificial seawater that suggest diffusion is several magnitude lower compared to a pure NaCl test. In practice marine exposure is always regarded as more severe and this is reflected in EN 206-1 and BS 8500-1:2006.

iv. The study has explored the possibility of establishing relationship of CEN TS 12390-11:2010 to a suitable rapid test method. Although this has so far only limited at ranking performance, it should in the future extended to an empirical D value relationship with the intention of finding a faster and easier way to estimate performance.

v. A set of highway exposed specimens were placed on the side of highway A928 near Dundee with the intention of retrieving them on a periodical basis to test for chloride ingress. The obvious recommendation is to retrieve and test these specimens for chloride performance at a later age and investigate the effects of ageing as time progresses and to use them as inputs to improve upon service life models.

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APPENDICES

APPENDIX A

Mix code reference showing simplified coding for thesis and the original mix code used during the concrete mixing process

Mix code	EN 197 notation	Proportions	Original Mix code
Reference mix			
R(D2)	CIIB-V	70% PC + 30% FA	ZR_.50 29/4
XD Classes mix			
D1	CEM I	100% PC	ZD_.40 26/1
D2	CIIB-V	70% PC + 30% FA	ZR_.50 29/4
D3	CIVB-V	50% PC + 50% FA	ZD_.55 18/2
D4	CIIIA	50% PC + 50% GGBS	ZD_.50 6/4
D5	CIIIB	30% PC + 70% GGBS	ZD_.55 24/2
D6	CIIA-D	92% PC + 8% SF	ZD_.40 6/7
D7	CIIA-LL	85% PC + 15% Limestone	ZD_.40 3/8
D8	CV/A-M (V-LL)	60% PC + 10% Limestone + 30% FA	ZS_.50 9/8
D9	CV/A-M (S-D)	46% PC + 46% GGBS + 8% SF	ZS_.40 13/7
D10	CV/A-M (S-LL)	43% PC+ 7% Limestone + 50% GGBS	ZD_.55 7/4
XS Classes mix			
S1	CEM I	100% PC	ZD_.35 7/4
S2	CIIB-V	70% PC + 30% FA	ZR_.50 29/4
S3	CIVB-V	50% PC + 50% FA	ZS_.50 5/5
S4	CIIIA	50% PC + 50% GGBS	ZD_.50 6/4
S5	CIIIB	30% PC + 70% GGBS	ZS_.50 6/5
S6	CIIA-D	92% PC + 8% SF	ZS_.35 15/7
S7	CIIA-LL	85% PC + 15% Limestone	ZS_.35 2/6
S8	CV/A-M (V-LL)	60% PC + 10% Limestone + 30% FA	ZS_.50 9/8
S9	CV/A-M (S-D)	46% PC + 46% GGBS + 8% SF	ZS_.40 13/7
S10	CV/A-M (S-LL)	43% PC+ 7% Limestone + 50% GGBS	ZD_.55 7/4
Series two, adjusted for characteristic strength;			
T1	CIVB-V	50% PC + 50% FA	ZD_.40 4/8C
T2	CIIIB	30% PC + 70% GGBS	ZD_.40 4/8A
T3	CIVB-V	50% PC + 50% FA	ZS_.40 4/8B
T4	CIIIA	50% PC + 50% GGBS	ZD_.45 9/8

Note: D2=S2; D4=S4;D8=S8;D9=S9;D10=S10

This information is intended for locating the mix design and test performance in Appendix E and Appendix F

APPENDIX B

Published NT Build 492 results analysed in Figure 2.13

Reference	Binder family	w/c	Total binder content, kg/m³	Aggregate content, kg/m³	Admixture wt of cement, %	Compressive strength, MPa	Age of testing, days	Average D_{nssm}, × 10^{-12} m²/s
(Tang and Sørensen, 2001)	CIIA-D	0.4	420	1860	0.8	82.6	28	3.105
	CEM I	0.5	380	1860	-	63.2	28	18.61
	CIIIB	0.5	390	1860	-	45.1	28	2.54
(Baroghel-Bouny et al., 2002a)	CEM I	0.84	230	1906	-	25.1	-	-
	CIVB	0.48	400	1860	4.8	28.9	-	-
	CEM I	0.65	306	1843	-	31.7	-	-
	CEM I	0.54	340	1891	air entraining	43.3	-	-
	CEM I	0.62	300	1898	-	44.1	-	-
	CEM I	0.49	353	1936	-	49.7	-	-
	CEM I	0.48	410	1743	-	55.5	-	-
	CEM I	0.44	370	1874	0.41	63	-	-
	CEM I	0.34	425	1912	5.95	68.8	-	-
	CIIA-D	0.36	382	1921	12	85.5	-	-
	CIVB	0.25	520	1905	14.16	87	-	-
	CIIA-D	0.28	480	1845	11.25	91.9	-	-
	CIIA-D	0.3	415	1920	12.5	109	-	-
(Salta and Ribeiro, 2002)	CEM I	0.65	260	1900	2.51	36.9	28	40.9
	CEM I	0.5	300	1913	3.60	49.6	28	15.4
	CEM I	0.45	340	1869	4.11	52.9	28	21.3
	CIIA-D	0.3	580.7	1637	13.3	80.7	28	2.7
	CIVB	0.65	260	1867	2.51	32.4	28	41.6

Cont'd…

cont'd…

Reference	Binder family	w/c	Total binder content, kg/m³	Aggregate content, kg/m³	Admixture wt of cement, %	Compressive strength, MPa	Age of testing, days	Average D_{nssm}, × 10^{-12} m^2/s
Salta And Ribeiro, cont'd…	CIVB	0.5	300	1875	3.60	46.4	28	11
	CIVB	0.45	340	1830	4.11	52.5	28	10.8
	CIVB, SF	0.3	580.7	1572	13.3	76.2	28	1.3
(Ferreira et al., 2004)	CIIIB	0.45	420	-	-	57.1	28	6.65
	CIIIA	0.45	420	-	-	64	28	5.6
	CIVA	0.45	420	-	-	53.9	28	13
	CIIIA	0.45	420	-	-	55.1	28	13.3
	CIIA-D (propriety)	0.45	420	-	-	78.7	28	8.05
	CEM I	0.45	420	-	-	55.6	28	11.9
	CIIIB	0.45	420	-	-	57.1	90	2.8
	CIIIA	0.45	420	-	-	64	90	4.55
	CIVA	0.45	420	-	-	53.9	90	5.95
	CIIIA	0.45	420	-	-	55.1	90	11.2
	CIIA-D (propriety)	0.45	420	-	-	78.7	90	3.5
	CEM I	0.45	420	-	-	55.6	90	12.95
	CIIIB	0.45	420	-	-	62.9	180	1.05
	CIIIA	0.45	420	-	-	81.2	180	1.75
	CIVA	0.45	420	-	-	61	180	3.5
	CIIIA	0.45	420	-	-	78.6	180	10.85
	CIIA-D (propriety)	0.45	420	-	-	-	180	1.05
	CEM I	0.45	420	-	-	72.3	180	11.9

Cont'd…

cont'd…

Reference	Binder family	w/c	Total binder content, kg/m³	Aggregate content, kg/m³	Admixture wt of cement, %	Compressive strength, MPa	Age of testing, days	Average D_{nssm}, × 10^{-12} m^2/s
(Romer et al., 2005)	CEM I	0.4	387	1910	1.7	62.7	150	14.2
	CEM I	0.55	320	1910	0.8	48.5	150	33.4
	CEM I	0.6	303	1910	0.3	34.4	150	57.1
	CIIIB	0.4	380	1910	0.9	52.4	150	3.9
	CIIIB	0.55	315	1910	0.5	38.2	150	5.5
	CEM I	0.55	320	1910	0.8	42.7	150	41.2
	CEM I	0.4	387	1910	1.7	63.6	150	16.5
	CEM I	0.55	320	1910	0.5	47.9	150	43.3
	CEM I	0.4	387	1910	1.7	63.5	150	13.9
	CEM I	0.55	320	1910	0.7	42.8	150	41.3
(Litorowicz, 2006)	CEM I	0.54	331	2008	-	45.8	28	6.05
	CIIB-V	0.54	332	2013	-	35.19	28	3.21
	CIIIA	0.54	331	2008	-	41.7	28	3.28
(Castellote et al., 2006)	CEM I - SF	0.4	399	1685	3.4	63	100	2.465
	CEM I	0.45	400	1772	4.8	45	100	12.400
	CIVB	0.45	340	1823	4.1	52.6	100	5.1534
	CIIIB	0.45	350	1830	3.9	-	100	2.485

Cont'd…

cont'd…

Reference	Binder family	w/c	Total binder content, kg/m³	Aggregate content, kg/m³	Admixture wt of cement, %	Compressive strength, MPa	Age of testing, days	Average D_{nssm}, × 10^{-12} m²/s
(Baroghel-Bouny et al., 2007a)	CIIA-V	0.67	238	1856	-	20.5	28	5.8
	CIIA-V	0.77	243	1897	-	23.5	28	9.5
	CEM I	0.84	230	2136	-	24.5	28	10
	CEM I	0.7	230	1888	-	26.8	28	22.4
	CIIB-V	0.52	318	1865	1.1	48.5	28	1.7
	CIIA-V	0.36	535	1513	-	49	28	1.5
	CEM I	0.39	483	1599	-	49.5	28	5.5
	CIIA-V	0.45	404	1405	-	53	28	1.8
	CEM I	0.48	410	1743	-	55.5	28	8.7
	CIIA-D	0.32	410	1809	12.9	67	28	0.73
	CEM I	0.27	557	1602	14.8	68.5	28	3.5
	CEM I	0.32	461	1833	12.4	75	28	5.6
	CIIA-D	0.36	382	1921	12	85.5	28	0.79
	CIIA-D	0.3	415	1920	12.5	109	28	0.3
	CIIA-D	0.23	527	1811	15.6	127.5	28	0.04

Note:
-, value not reported

APPENDIX C

Published C_s and D_{nss} values from laboratory experiments analysed in Figure 2.16

Reference	Method	Cement	C_s, Cement	D_{nss}, 1×10^{-12} m^2/s	Age, month	Cement content, kg/m^3	w/c	Contact solution, % NaCl
(Mangat and Molloy, 1994)+	Acid soluble	CEM I	1.5	29	1	430	0.58	3
		"	1.1	14	1	430	0.45	3
		"	1.4	25	1	530	0.58	3
		FA25%	2.2	18	1	430	0.58	3
		ggbs 60%	2	28	1	430	0.58	3
		SF 15%	1.2	20	1	430	0.58	3
(Andrade and Whiting, 1995)	AASHTO T-259	CEM I	3.2	24.56	1	390	0.6	3
		"	4.62	7.9	1	390	0.4	3
		"	2.3	4.2	1	490	0.32	3
(Hong and Hooton, 1999)§	Bulk diffusion	ggbs 25%	N.R.	3.46	1	380	0.40	5.84
		ggbs 25 – SF 8%	N.R.	1.42	1	380	0.40	5.84
		ggbs 25 – SF 8	N.R.	0.74	1	460	0.30	5.84
(Tang and Sørensen, 2001)	NT Build 443	SF 8%	N.R.	3.733	1.25	420	0.40	16.5
		SRPC	N.R.	16.061	1.25	380	0.50	16.5
		ggbs 70%	N.R.	2.05	1.25	390	0.50	16.5
(Bleszynski et al., 2002)*	ASTM C-114	CEM I	5.37	8.5	1	420	0.42	17.53
	NT Build 443	SF 8%	5.26	1	1	420	0.42	17.53
		ggbs 35%	6.11	2	1	420	0.42	17.53
		ggbs 50%	7.2	2.5	1	420	0.42	17.53
		SF 4% - ggbs 25%	4.74	1.5	1	420	0.42	17.53
		SF 6% - ggbs 25%	4.06	1	1	420	0.42	17.53
		SF 5.2% - ggbs 35%	3.66	0.8	1	420	0.42	17.53
		CEM I	5.71	8.4	24	420	0.42	17.53
		SF 8%	5.14	2.9	24	420	0.42	17.53

Cont'd…

cont'd…

Reference	Method	Cement	C_s, Cement	D_{nss}, 1×10^{-12} m^2/s	Age, month	Cement content, kg/m^3	w/c	Contact solution, % NaCl
(Bleszynski et al., cont'd…		ggbs 35%	9.54	1.8	24	420	0.42	17.53
		ggbs 50%	8.34	1.1	24	420	0.42	17.53
		SF 4% - ggbs 25%	7.26	1	24	420	0.42	17.53
		SF 6% - ggbs 25%	7.49	1.3	24	420	0.42	17.53
		SF 5.2% - ggbs 35%	8.34	0.9	24	420	0.42	17.53
(Stanish and Thomas, 2003)	NT Build 443	CEM I	2.88	5.53	3	300	0.5	16.5
		FA 25%	0.56	1.56	3	300	0.5	16.5
		FA 56%	3.2	1.53	3	300	0.5	16.5
(Castellote et al., 2006)	NT Build 443	SF 5%	N.R.	2.212	3	430	0.40	16.5
		CEM I	N.R.	19.39	3	400	0.45	16.5
		FA 39%	N.R.	7.115	3	340	0.45	16.5
		ggbs 76%	N.R.	2.629	3	350	0.45	16.5
(Baroghel-Bouny et al., 2007b)	AFPC-AFREM	CEM I	2.43	N.R	3	230	0.84	1.82
		"	1.74	N.R	3	353	0.49	1.82
(Elahi et al., 2010)[¥]	NT Build 443	100% PC	0.9	3.1	n.r.	485	0.3	16.5
		SF 7.5%	1.13	0.87	n.r.	485	0.3	16.5
		SF 15%	1.06	0.76	n.r.	485	0.3	16.5
		GGBS 50%	1.17	1	n.r.	485	0.3	16.5
		GGBS 70%	1	0.83	n.r.	485	0.3	16.5
		SF 7.5%, GGBS 50%	2.07	0.2	n.r.	485	0.3	16.5
		FA 20%	1.18	1.18	n.r.	485	0.3	16.5
		FA 40%	1.19	1.19	n.r.	485	0.3	16.5
		SF 7.5%, FA 20%	1.06	0.7	n.r.	485	0.3	16.5
		SF 7.5%, FA 40%	1.04	0.54	n.r.	485	0.3	16.5

Cont'd…

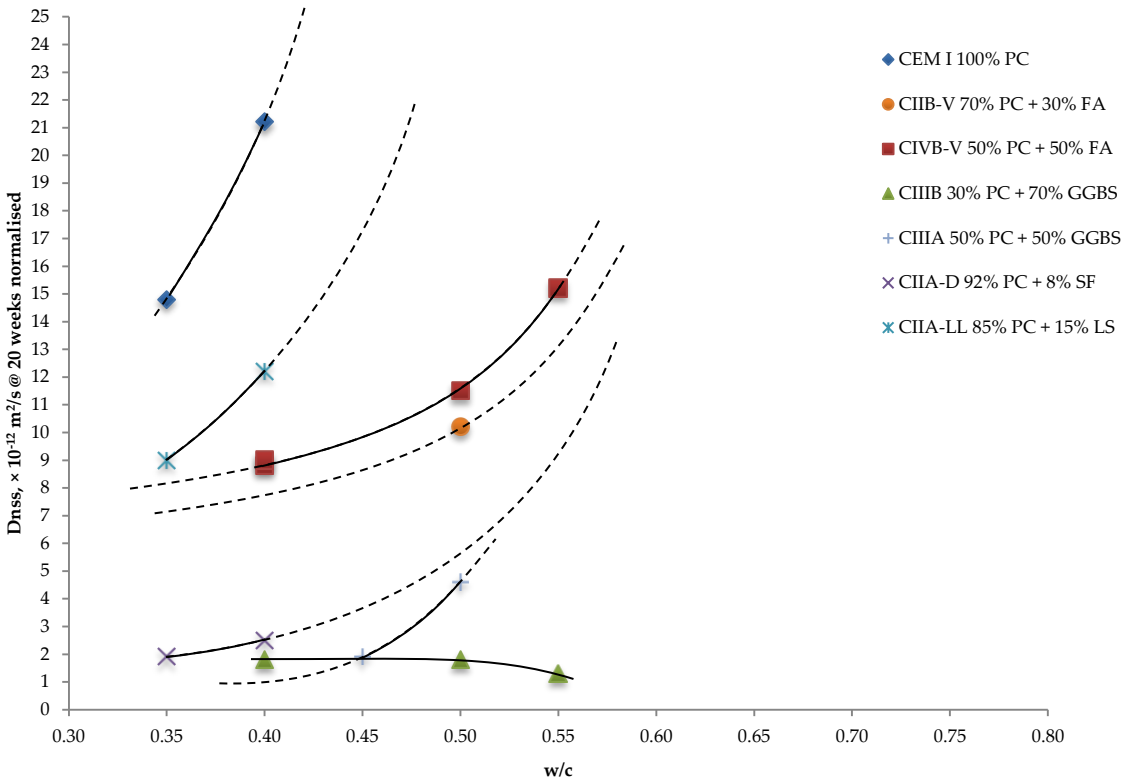
cont'd…

Reference	Method	Cement	C_s, Cement	D_{nss}, 1×10^{-12} m^2/s	Age, month	Cement content, kg/m^3	w/c	Contact solution, % NaCl
(Andrade et al., 2011)	AASHTO T 259	CEM I	2.14	21	4	400	0.45	3
		"	1.34	32.2	15	400	0.45	3
		"	2.62	57.9	24	400	0.45	3
		"	2.56	22	30	400	0.45	3
		"	2.32	48.6	36	400	0.45	3
		FA 35%	2.14	4.4	4	400	0.45	3
		"	1.22	4.32	13	400	0.45	3
		"	1.59	1.57	24	400	0.45	3
		"	3.05	0.83	30	400	0.45	3
		"	2.56	0.58	36	400	0.45	3
		SF 9%	1.89	10.8	4	400	0.45	3
		"	1.28	7.02	13	400	0.45	3
		"	2.2	6.97	30	400	0.45	3
		FA 35% - SF 9%	1.28	2.17	4	400	0.56	3
		"	1.52	1.51	13	400	0.56	3
		"	1.4	0.95	24	400	0.56	3

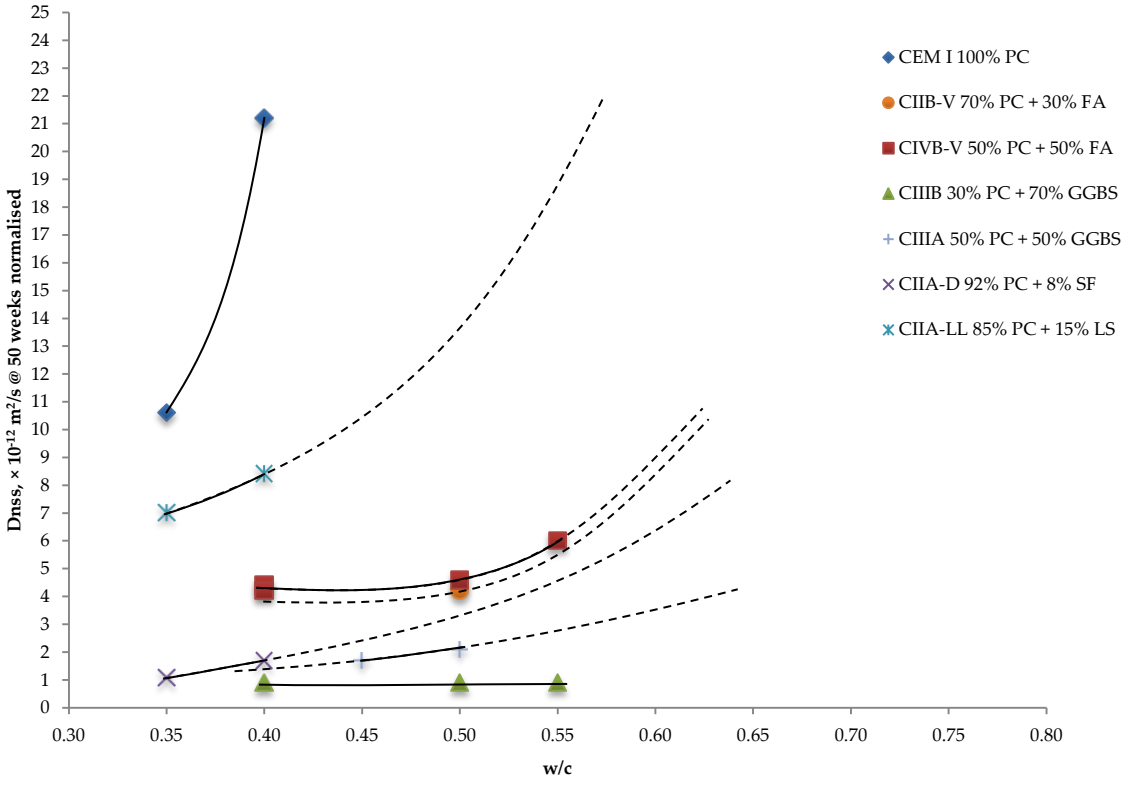
+ Exposure solution is seawater in internal tank
* Exposure period is 40 days instead of the standard 90 days
§ Cyclic exposure
¥ Curing is 3 days water, then wrapped in polythene sheet and placed in 55% humidity chamber, 20 °C
" Same as above
n.r. Not reported

APPENDIX D

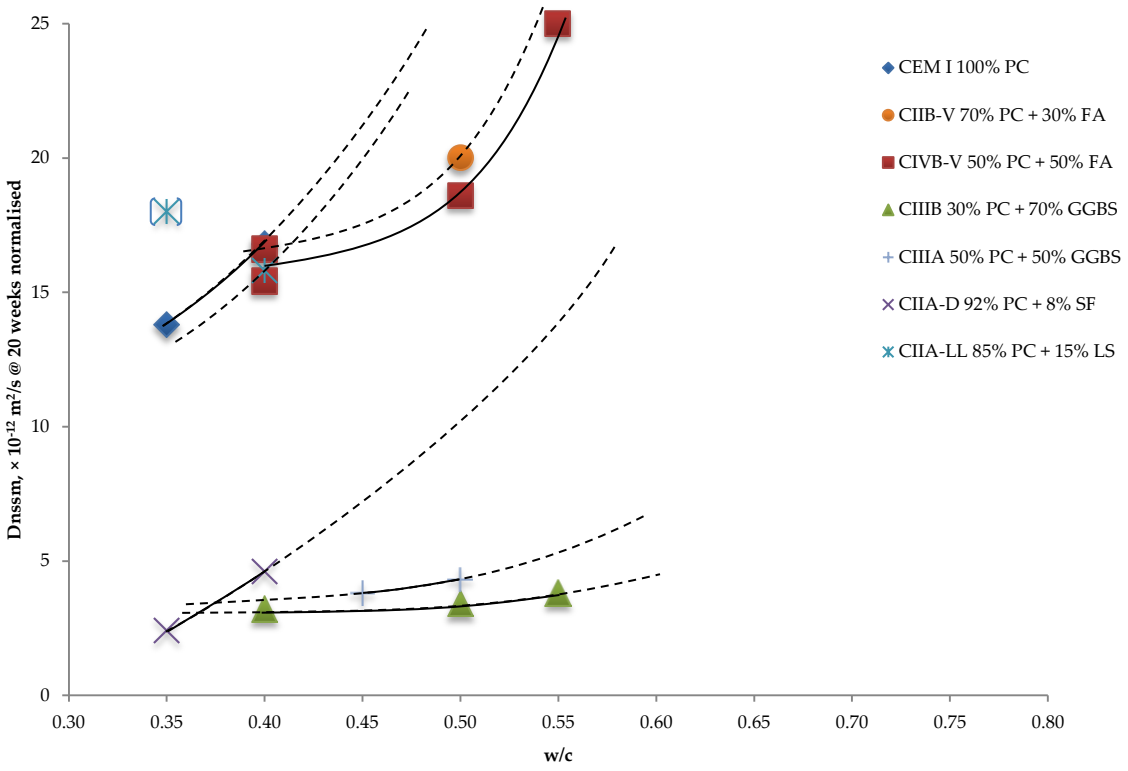
Figures used for normalisation of concrete performance to 40 N/mm^2, 50 N/mm^2 and 0.45 w/c



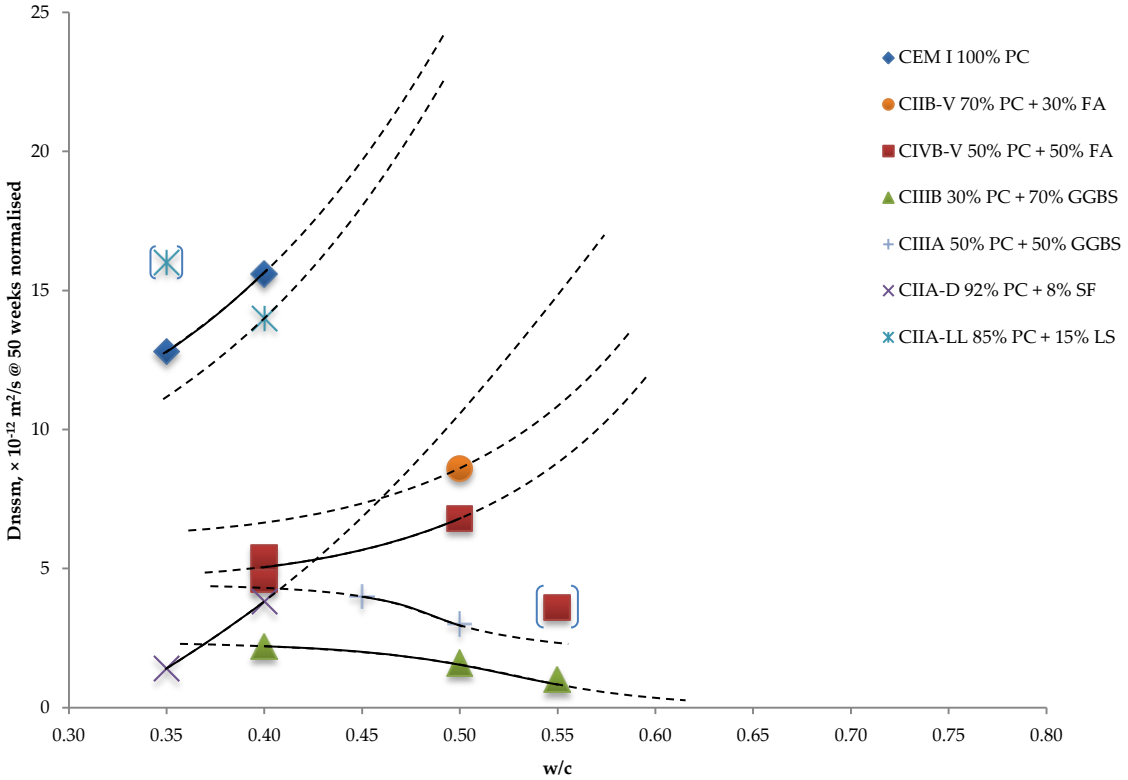
Performance of concrete at 20 weeks test age with CEN TS 121390-11



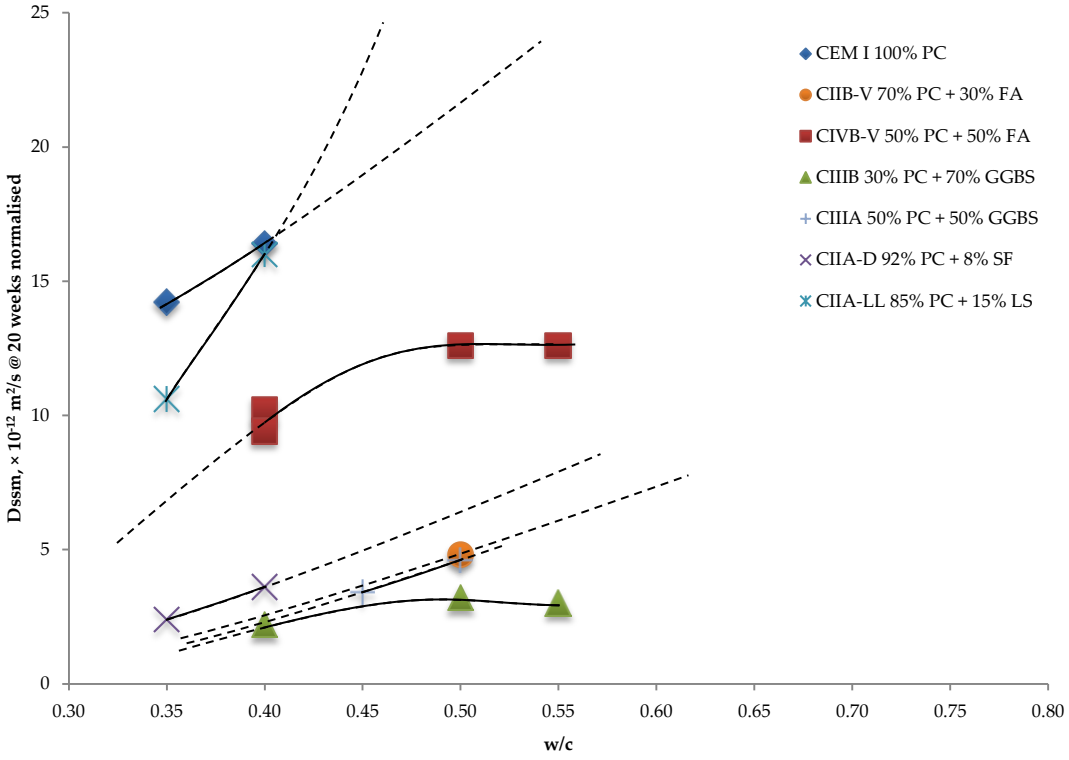
Performance of concrete at 50 weeks test age with CEN TS 121390-11



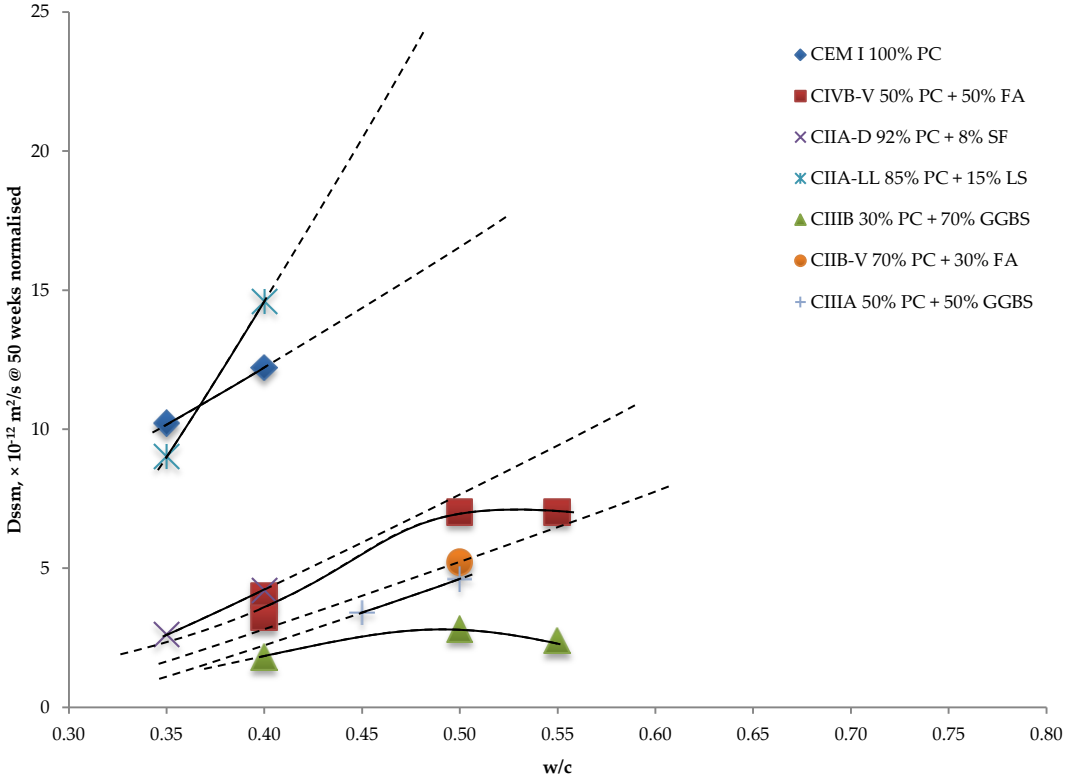
Performance of concrete at 20 weeks test age with NT Build 492



Performance of concrete at 50 weeks test age with NT Build 492



Performance of concrete at 20 weeks test age with Multi-Regime test



Performance of concrete at 50 weeks test age with Multi-Regime test

APPENDIX E

Raw data for CEN TS 12390-11:2010

V4, Volume of AgNo3 in Blank 0.0583

f, Molarity of AgNo3 0.1

Sample name: CEM I, 100% CEM I

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 26/1 S1 16/6/10+			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0071		1.3202	**0.4442***
3	**2**	2	1.0048		1.1887	**0.3988**
5	**4**	3	1.0117		1.0998	**0.3649**
7	**6**	4	1.0012		1.0039	**0.3348**
10	**8.5**	5	1.0011		0.7317	**0.2384**
13	**11.5**	6	1.0033		0.5331	**0.1678**
16	**14.5**	7	1.0052		0.3805	**0.1136**
20	**18**	8	1.011		0.2418	**0.0643**
ZD1.4 26/1 S2 16/6/10						
1	**0.5**	1	1.0079		0.9436	**0.3114**
3	**2**	2	1.0042		0.9793	**0.3251**
5	**4**	3	1.0106		1.0554	**0.3498**
7	**6**	4	1.008		0.9526	**0.3145**
10	**8.5**	5	1.0089		0.7572	**0.2456**
13	**11.5**	6	1.0027		0.5264	**0.1655**
16	**14.5**	7	1.0057		0.38	**0.1134**
20	**18**	8	1.0094		0.2375	**0.0629**
ZD1.4 26/1 S1 10/11/10			Exposure, t=	90	Ci=	
1	0.5	1	1.0081		1.2299	**0.4120**
3	2	2	1.0038		1.1964	**0.4019**
5	4	3	1.0093		1.1686	**0.3900**
7	6	4	1.0018		1.1685	**0.3928**
10	8.5	5	1.0067		1.0231	**0.3397**
13	11.5	6	1.0098		0.8769	**0.2874**
16	14.5	7	1.0088		0.757	**0.2455**
20	18	8	1.0033		0.5771	**0.1833**
ZD1.4 26/1 S2 10/11/10			Exposure, t=	90	Ci=	
1	0.5	1	1.0046		1.1691	**0.3920**
3	2	2	1.0065		1.1767	**0.3939**
5	4	3	1.0082		1.1594	**0.3872**
7	6	4	1.0041		1.0973	**0.3668**
10	8.5	5	1.004		0.9061	**0.2993**
13	11.5	6	1.0065		0.8098	**0.2647**
16	14.5	7	1.006		0.6392	**0.2047**
20	18	8	1.0059		0.4183	**0.1269**

+Mix notation ZD[batch number.w/c]_[cast date]_[sample number]_[profile grinding date]

** Values in red not included in regression analysis.*

Sample name: CEM I, 100% **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 26/1 S3 10/11/10			Exposure, t=	90	Ci=	
1	0.5	1	1.0076		1.1731	**0.3922**
3	2	2	1.0032		1.1912	**0.4003**
5	4	3	1.0085		1.1899	**0.3978**
7	6	4	1.005		1.142	**0.3822**
10	8.5	5	1.0024		1.1276	**0.3781**
13	11.5	6	1.0086		1.0645	**0.3536**
16	14.5	7	1.0031		0.705	**0.2285**
20	18	8	1.0049		0.4716	**0.1458**
ZD1.4 26/1 S1 20/1/2011			Exposure, t=	92	Ci=	
1	0.5	1	1.0094		1.2668	**0.4244**
3	2	2	1.009		1.2086	**0.4041**
5	4	3	1.0034		1.0842	**0.3624**
7	6	4	1.0067		0.893	**0.2939**
10	8.5	5	1.0099		0.8329	**0.2719**
13	11.5	6	1.0076		0.6922	**0.2230**
16	14.5	7	1.0045		0.5198	**0.1629**
20	18	8	1.0075		0.2863	**0.0802**
ZD1.4 26/1 S2 20/1/2011			Exposure, t=	92	Ci=	
1	0.5	1	1.0079		1.3299	**0.4472**
3	2	2	1.0075		1.1933	**0.3994**
5	4	3	1.004		1.1409	**0.3822**
7	6	4	1.0027		1.0694	**0.3575**
10	8.5	5	1.0032		1.0197	**0.3397**
13	11.5	6	1.0097		0.8328	**0.2719**
16	14.5	7	1.0092		0.6444	**0.2059**
20	18	8	1.0069		0.5384	**0.1690**
ZD1.4 26/1 S3 20/1/2011			Exposure, t=	92	Ci=	
1	0.5	1	1.0068		1.3016	**0.4378**
3	2	2	1.0089		1.2166	**0.4070**
5	4	3	1.0049		1.1407	**0.3818**
7	6	4	1.0033		0.9481	**0.3144**
10	8.5	5	1.0062		0.8121	**0.2656**
13	11.5	6	1.0073		0.7694	**0.2502**
16	14.5	7	1.0028		0.6953	**0.2252**
20	18	8	1.0043		0.4351	**0.1330**

Sample name: CEM I, 100% **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 26/1 S1 2/6/11 XS			Exposure, t=	90	Ci=	
1	0.5	1	1.002		0.3186	**0.0921**
3	2	2	1.0083		0.2081	**0.0527**
5	4	3	1.0024		0.1551	**0.0342**
7	6	4	1.0071		0.1365	**0.0275**
10	8.5	5	1.0083		0.0928	**0.0121**
13	11.5	6	1.006		0.0799	**0.0076**
16	14.5	7	1.0054		0.0757	**0.0061**
20	18	8	1.002		0.0647	**0.0023**
ZD1.4 26/1 S2 2/6/11 XS			Exposure, t=	90	Ci=	
1	0.5	1	1.0017		0.5763	**0.1833**
3	2	2	1.005		0.2423	**0.0649**
5	4	3	1.0064		0.1868	**0.0453**
7	6	4	1.0017		0.1631	**0.0371**
10	8.5	5	1.0063		0.111	**0.0186**
13	11.5	6	1.0021		0.1054	**0.0167**
16	14.5	7	1.0072		0.0782	**0.0070**
20	18	8	1.0052		0.0574	**0.0003**
ZD1.4 26/1 S3 2/6/11 XS			Exposure, t=	90	Ci=	
1	0.5	1	1.0032		0.555	**0.1755**
3	2	2	1.0069		0.3236	**0.0934**
5	4	3	1.001		0.2567	**0.0703**
7	6	4	1.0047		0.1419	**0.0295**
10	8.5	5	1.0028		0.1633	**0.0371**
13	11.5	6	1.0055		0.1165	**0.0205**
16	14.5	7	1.0017		0.0866	**0.0100**
20	18	8	1.0063		0.0713	**0.0046**

Sample name: CIVB-V 50% CEM I+ 50% FA

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.55 18/2 S1 22/7			Exposure, t=	90	Ci=	
1.5	**0.75**	1	0.998		0.7786	**0.2558**
4.4	**2.95**	2	0.9989		0.8414	**0.2779**
6.3	**5.35**	3	1.0025		0.8847	**0.2922**
8.2	**7.25**	4	1.0032		0.8826	**0.2912**
11	**9.6**	5	1.0055		0.7274	**0.2358**
14	**12.5**	6	1.0085		0.5755	**0.1817**
16.7	**15.35**	7	1.0085		0.4157	**0.1256**
19	**17.85**	8	1.0086		0.3598	**0.1059**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.55 18/2 S2 22/7			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0009		1.1052	**0.3707**
2.4	**1.7**	2	1.0039		0.99	**0.3289**
3.3	**2.85**	3	0.9969		1.0029	**0.3358**
5.3	**4.3**	4	1.0002		1.006	**0.3358**
7.3	**6.3**	5	0.9996		0.9454	**0.3145**
10.3	**8.8**	6	1.0001		0.7318	**0.2387**
14.6	**12.45**	7	1.0039		0.6425	**0.2062**
18.7	**16.65**	8	0.9978		0.5015	**0.1574**
ZD 1.55 18/2 S3 22/7			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0053		1.3716	**0.4630**
2	**1.5**	2	1.0101		0.9994	**0.3302**
3.6	**2.8**	3	1		0.9693	**0.3229**
6.3	**4.95**	4	1.0045		0.9858	**0.3273**
10	**8.15**	5	0.9962		0.7707	**0.2534**
13	**11.5**	6	0.9976		0.6363	**0.2053**
15.8	**14.4**	7	1.0003		0.516	**0.1621**
18.5	**17.15**	8	1.0088		0.4526	**0.1385**
ZD2.55 18/2 S1 11/11/10			Exposure, t=	99	Ci=	
1	**0.5**	1	1.0091		0.6922	**0.2226**
3	**2**	2	1.0037		0.8124	**0.2663**
5	**4**	3	1.0011		0.837	**0.2757**
7	**6**	4	1.0088		0.7451	**0.2413**
10	**8.5**	5	1.0054		0.6209	**0.1983**
13	**11.5**	6	1.0027		0.4982	**0.1555**
16	**14.5**	7	1.002		0.4147	**0.1260**
20	**18**	8	1.0102		0.3302	**0.0954**
ZD2.55 18/2 S2 11/11/10			Exposure, t=	99	Ci=	
1	**0.5**	1	1.0048		0.7214	**0.2339**
3	**2**	2	1.0045		0.8569	**0.2818**
5	**4**	3	1.0061		0.8346	**0.2735**
7	**6**	4	1.0076		0.7597	**0.2467**
10	**8.5**	5	1.0048		0.6473	**0.2077**
13	**11.5**	6	1.0013		0.5182	**0.1628**
16	**14.5**	7	1.0088		0.3585	**0.1054**
20	**18**	8	1.0034		0.317	**0.0913**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD2.55 18/2 S3 11/11/10			Exposure, t=	99	Ci=	
1	**0.5**	1	1.0055		0.7565	**0.2461**
3	**2**	2	1.0075		0.7463	**0.2420**
5	**4**	3	1.0043		0.8788	**0.2896**
7	**6**	4	1.0064		0.7984	**0.2606**
10	**8.5**	5	1.0009		0.5128	**0.1609**
13	**11.5**	6	1.0019		0.4473	**0.1376**
16	**14.5**	7	1.0033		0.4212	**0.1282**
20	**18**	8	1.0084		0.3255	**0.0939**
ZD1.55 18/2 S1 20/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0035		0.6769	**0.2185**
3	**2**	2	1.0096		0.6411	**0.2046**
5	**4**	3	1.0064		0.616	**0.1964**
7	**6**	4	1.0082		0.5058	**0.1573**
10	**8.5**	5	1.0079		0.4002	**0.1202**
13	**11.5**	6	1.003		0.2707	**0.0750**
16	**14.5**	7	1.0089		0.2379	**0.0630**
20	**18**	8	1.0026		0.1575	**0.0350**
ZD1.55 18/2 S2 20/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0095		0.6471	**0.2067**
3	**2**	2	1.0031		0.6037	**0.1927**
5	**4**	3	1.0094		0.5296	**0.1655**
7	**6**	4	1.0091		0.497	**0.1541**
10	**8.5**	5	1.0044		0.4229	**0.1286**
13	**11.5**	6	1.0076		0.3325	**0.0964**
16	**14.5**	7	1.0052		0.2112	**0.0539**
20	**18**	8	1.0021		0.1311	**0.0257**
ZD1.55 18/2 S3 20/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0093		0.9395	**0.3094**
3	**2**	2	1.0032		0.5694	**0.1805**
5	**4**	3	1.0077		0.5356	**0.1678**
7	**6**	4	1.0096		0.5129	**0.1596**
10	**8.5**	5	1.0092		0.3774	**0.1120**
13	**11.5**	6	1.0014		0.3196	**0.0924**
16	**14.5**	7	1.0074		0.2172	**0.0559**
20	**18**	8	1.009		0.1816	**0.0433**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
Z2 2.55 18/2 S1 9/6/11			Exposure, t=	98	Ci=	
1	**0.5**	1	1.0998		1.0179	**0.3092**
3	**2**	2	1.0908		0.7464	**0.2236**
5	**4**	3	1.1171		0.7587	**0.2222**
7	**6**	4	1.0716		0.5482	**0.1620**
10	**8.5**	5	1.1171		0.4623	**0.1281**
13	**11.5**	6	1.0647		0.2077	**0.0497**
16	**14.5**	7	1.0506		0.1396	**0.0274**
20	**18**	8	1.1		0.1225	**0.0206**
Z2 2.55 18/2 S1 9/6/11			Exposure, t=	98	Ci=	
1	**0.5**	1	1.0465		0.9858	**0.3141**
3	**2**	2	1.0613		0.6999	**0.2142**
5	**4**	3	1.1962		0.7431	**0.2029**
7	**6**	4	1.0293		0.5544	**0.1708**
10	**8.5**	5	1.134		0.395	**0.1052**
13	**11.5**	6	1.1887		0.3366	**0.0829**
16	**14.5**	7	1.0101		0.1734	**0.0403**
20	**18**	8	1.1661		0.1057	**0.0144**
Z2 2.55 18/2 S1 9/6/11			Exposure, t=	99	Ci=	
1	**0.5**	1	1.1505		0.832	**0.2383**
3	**2**	2	1.0932		0.6474	**0.1910**
5	**4**	3	1.0586		0.647	**0.1971**
7	**6**	4	1.0955		0.5445	**0.1573**
10	**8.5**	5	1.0154		0.323	**0.0924**
13	**11.5**	6	1.0339		0.2431	**0.0633**
16	**14.5**	7	1.0534		0.1312	**0.0245**
20	**18**	8	1.1407		0.1145	**0.0174**

Sample name: CIIIB, 30% CEM I + 70% ggbs

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.55 24/2 S1 22/7			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0042	A	1.5084	**0.5118**
2	**1.5**	2	1.0097	B	1.2425	**0.4157**
3.6	**2.8**	3	0.9987	C	0.8986	**0.2982**
5.5	**4.55**	4	1.0066	D	0.5862	**0.1859**
8.5	**7**	5	1.01	E	0.2138	**0.0545**
12.2	**10.35**	6	1.0099	F	0.0583	**0.0001**
15.4	**13.8**	7	1.0057	G	0.058	**0.0001**
18.7	**17.05**	8	1.0041	H	0.057	**0.0004**

Sample name: CIIIB, 30% CEM I + 70% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams			V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.55 24/2 S2 22/7			Exposure, t=		90	Ci=	
1.5	**0.75**	1	0.9991	AV		2.6756	**0.9286**
2.3	**1.9**	2	1.0015	AW		1.3555	**0.4591**
3.9	**3.1**	3	1.0059	AX		1.0231	**0.3400**
6	**4.95**	4	1.0043	AY		0.6208	**0.1985**
9.5	**7.75**	5	0.9999	AZ		0.2624	**0.0723**
11.6	**10.55**	6	1.0049	BA		0.0838	**0.0089**
14.5	**13.05**	7	0.9992	BB		0.0682	**0.0040**
18.8	**16.65**	8	0.9999	BC		0.055	**0.00**
ZD 1.55 24/2 S3 22/7			Exposure, t=		90	Ci=	
0.8	**0.4**	1	0.9989	AO		2.771	**0.9626**
1.7	**1.25**	2	0.9982	AP		1.1568	**0.3901**
4	**2.85**	3	1.0022	AQ		0.8921	**0.2949**
6	**5**	4	1	AR		0.5301	**0.1672**
9	**7.5**	5	1.0003	AS		0.2636	**0.0727**
12	**10.5**	6	1.0046	AT		0.0978	**0.0139**
15	**13.5**	7	1.0064	AU		0.0622	**0.0013**
18	**16.5**	8	1.004			0.0552	**0.0011**
ZD 1.55 24/2 S3 22/7 Repeat 1			Exposure, t=		90	Ci=	
0.8	**0.4**	1	1.0213			2.2904	**0.7747**
1.7	**1.25**	2	1.0212			1.2007	**0.3965**
4	**2.85**	3	1.017			0.9021	**0.2941**
6	**5**	4	1.0013			0.4955	**0.1547**
9	**7.5**	5	1.0041			0.2631	**0.0722**
12	**10.5**	6	1.0095			0.1033	**0.0157**
15	**13.5**	7	1.012			0.0767	**0.0064**
18	**16.5**	8	1.0131			0.0655	**0.0025**
ZD2.55 25/2 S1 6/6/11			Exposure, t=		95	Ci=	
1	0.5	1	1.0084			1.0964	**0.3649**
3	2	2	1.0009			0.8297	**0.2732**
5	4	3	1.0065			0.5072	**0.1580**
7	6	4	1.0044			0.2732	**0.0758**
10	8.5	5	1.0059			0.084	**0.0090**
13	11.5	6	1.0064			0.0634	**0.0017**
16	14.5	7	1.0013			0.0656	**0.0025**
20	18	8	1.008			0.0548	**0.00**

Sample name: CIIIB, 30% CEM I + 70% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD2.55 25/2 S2 6/6/11			Exposure, t=	95	Ci=	
1	0.5	1	1.0085		1.1151	**0.3714**
3	2	2	1.0043		0.9819	**0.3260**
5	4	3	1.0044		0.5725	**0.1814**
7	6	4	1.0025		0.2426	**0.0651**
10	8.5	5	1.002		0.0703	**0.0042**
13	11.5	6	1.0038		0.0814	**0.0081**
16	14.5	7	1.0003		0.066	**0.0027**
20	18	8	1.0041		0.06	**0.00**

Sample name: CIIA, 50% CEM I + 50%ggbs

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.5 6/4 S1 30/8			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0124	1	1.6345	**0.5519**
3	**2**	2	1.0074	2	0.9962	**0.3300**
5	**4**	3	1.0034	3	0.8592	**0.2829**
7	**6**	4	1.0097	4	0.7096	**0.2286**
10	**8.5**	5	1.0104	5	0.4964	**0.1536**
13	**11.5**	6	1.0039	6	0.3364	**0.0981**
15.5	**14.25**	7	1.0047	7	0.1972	**0.0489**
19	**17.25**	8	1.0116	8	0.083	**0.0086**
ZD1.5 6/4 S2 31/8			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0008	AN	1.8706	**0.6419**
3	**2**	2	1.0057	AO	0.886	**0.2917**
5	**4**	3	1.0025	AP	0.8601	**0.2835**
7	**6**	4	1.0059	AQ	0.6305	**0.2016**
10	**8.5**	5	1.0059	AR	0.3821	**0.1141**
13	**11.5**	6	1.004	AS	0.2266	**0.0594**
16	**14.5**	7	1.004	AT	0.0963	**0.0134**
19.5	**17.75**	8	1.001	AU	0.0766	**0.0064**
ZD1.5 6/4 S3 31/8			Exposure, t=	90	Ci=	
1	**0.5**	1	0.9996	AF	4.4499	**1.5574**
3	**2**	2	0.9998	AG	0.9839	**0.3281**
5	**4**	3	1.0022	AH	0.8007	**0.2625**
7	**6**	4	1.0075	AI	0.6041	**0.1920**
9.7	**8.35**	5	1.004	AJ	0.4561	**0.1404**
13	**11.35**	6	1.0075	AK	0.2897	**0.0814**
16	**14.5**	7	1.0039	AL	0.1536	**0.0336**
19	**17.5**	8	1.0008	AM	0.0829	**0.0087**

Sample name: CIIA, 50% CEM I + 50%ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.5 6/4 S1 30/8 REPEAT			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0061		1.9173	**0.6550**
3	**2**	2	1.0052		0.9532	**0.3155**
5	**4**	3	1.0008		0.8565	**0.2827**
7	**6**	4	1		0.664	**0.2147**
10	**8.5**	5	1.0065		0.5039	**0.1569**
13	**11.5**	6	1.0028		0.3318	**0.0966**
15.5	**14.25**	7	1.0071		0.2117	**0.0539**
19	**17.25**	8	1.0044		0.0648	**0.0022**
ZD 1.5 6/4 S1 24/6			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0845		1.0927	**0.3381**
3	**2**	2	1.0596		0.8748	**0.2731**
5	**4**	3	1.0215		0.639	**0.2015**
7	**6**	4	1.0187		0.4225	**0.1267**
10	**8.5**	5	1.0817		0.1743	**0.0380**
13	**11.5**	6	1.0038		0.0672	**0.0031**
16	**14.5**	7	1.0206		0.0723	**0.0048**
20	**18**	8	1.0808		0.0636	**0.0017**
ZD 1.5 6/4 S2 24/6			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0588		1.1632	**0.3699**
3	**2**	2	1.0166		0.9755	**0.3198**
5	**4**	3	1.0551		0.7584	**0.2352**
7	**6**	4	1.0448		0.506	**0.1518**
10	**8.5**	5	1.0819		0.2729	**0.0703**
13	**11.5**	6	1.03		0.097	**0.0133**
16	**14.5**	7	1.0975		0.062	**0.0011**
20	**18**	8	1.0645		0.0754	**0.0056**
ZD 1.5 6/4 S3 24/6			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0101		1.434	**0.4827**
3	**2**	2	1.098		1.2326	**0.3791**
5	**4**	3	1.016		0.8151	**0.2640**
7	**6**	4	1.032		0.4814	**0.1453**
10	**8.5**	5	1.0147		0.1828	**0.0434**
13	**11.5**	6	1.0785		0.0727	**0.0047**
16	**14.5**	7	1.0088		0.06	**0.0005**
20	**18**	8	1.02		0.0585	**0.0005**

Sample name: CIIA, 50% CEM I + 50%ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.5 6/4 S1 30/6 XS			Exposure, t=	120	Ci=	
1	**0.5**	1	1.0397		0.5522	**0.1683**
3.3	**2.15**	2	1.0199		0.1364	**0.0271**
5	**4.15**	3	1.0213		0.0882	**0.0103**
7	**6**	4	1.0521		0.0848	**0.0089**
10	**8.5**	5	1.0894		0.0599	**0.0005**
13	**11.5**	6	1.0746		0.052	**0.00**
16	**14.5**	7	1.0305		0.0594	**0.0003**
20	**18**	8	1.0105		0.062	**0.0012**
ZD 1.5 6/4 S1 30/6 XS			Exposure, t=	120	Ci=	
1	**0.5**	1	1.0202		0.9194	**0.2992**
3	**2**	2	1.0636		0.2457	**0.0624**
5	**4**	3	1.0144		0.0888	**0.0106**
7	**6**	4	1.0962		0.0528	**0.00**
10	**8.5**	5	1.0625		0.0563	**0.00**
13	**11.5**	6	1.047		0.055	**0.00**
16	**14.5**	7	1.0314		0	**0.00**
20	**18**	8	1.0294		0.061	**0.0009**
ZD 1.5 6/4 S1 30/6 XS			Exposure, t=	120	Ci=	
1	**0.5**	1	1.0264		1.8726	**0.6266**
3	**2**	2	1.0742		0.5062	**0.1478**
5	**4**	3	1.0485		0.2325	**0.0588**
7	**6**	4	1.0119		0.1647	**0.0372**
10	**8.5**	5	1.0491		0.1532	**0.0320**
13	**11.5**	6	1.0445		0.0842	**0.0087**
16	**14.5**	7	1.0481		0.0767	**0.0062**
20	**18**	8	1.0593		0.0732	**0.0049**

Sample name: Ternary blend 1, 43% CEM I +7% LS + 50% ggbs

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.55 7/4 S1 30/8			Exposure, t=	90	Ci=	
0.7	**0.35**	1	1.005	A	1.4182	**0.4796**
1.7	**1.2**	2	1.0074	B	1.306	**0.4390**
4.5	**3.1**	3	1.0092	C	1.331	**0.4470**
6.5	**5.5**	4	1.0117	D	0.8828	**0.2888**
9.5	**8**	5	1.0088	E	0.7659	**0.2486**
12.4	**10.95**	6	1.0121	F	0.622	**0.1974**
15.5	**13.95**	7	1.0047	G	0.4332	**0.1322**
19	**17.25**	8	1.0099	H	0.2918	**0.0819**

Sample name: Ternary blend 1, 43% CEM I +7% LS + 50% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams			V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.55 7/4 S2 30/8			Exposure, t=		90	Ci=	
1	**0.5**	1	1.0046	I		1.1059	**0.3696**
3.4	**2.2**	2	1.0093	J		0.8318	**0.2716**
5	**4.2**	3	1.0026	K		0.7765	**0.2539**
6.8	**5.9**	4	1.0093	L		0.6883	**0.2212**
10	**8.4**	5	1.0055	M		0.3861	**0.1155**
13.2	**11.6**	6	1.0089	N		0.108	**0.0174**
16	**14.6**	7	1.0079	O		0.1244	**0.0232**
19.4	**17.7**	8	1.0012	P		0.058	**0.00**
ZD1.55 7/4 S3 30/8			Exposure, t=		90	Ci=	
0.7	**0.35**	1	1.0064	Q		1.3583	**0.4579**
2.7	**1.7**	2	1.004	R		0.7778	**0.2540**
5	**3.85**	3	1.0037	S		0.6899	**0.2230**
7.6	**6.3**	4	1.0011	T		0.534	**0.1684**
9.5	**8.55**	5	1.0022	U		0.4026	**0.1217**
12	**10.75**	6	1.0122	V		0.221	**0.0569**
16	**14**	7	1.0096	W		0.1182	**0.0210**
19	**17.5**	8	1.0026	X		0.0869	**0.0101**
ZD1.55 7/4 S1 30/8 REPEAT			Exposure, t=		90	Ci=	
0.7	**0.35**	1	1.0169			1.3727	**0.4581**
1.7	**1.2**	2	1.0147			1.3308	**0.4445**
4.5	**3.1**	3	1.0054			1.128	**0.3771**
6.5	**5.5**	4	1.0117			0.9129	**0.2994**
9.5	**8**	5	1.0032			0.7624	**0.2487**
12.4	**10.95**	6	1.0169			0.6787	**0.2162**
15.5	**13.95**	7	1.0137			0.4501	**0.1370**
19	**17.25**	8	1.0073			0.2855	**0.0799**
ZD1.55 7/4 S2 30/8 REPEAT			Exposure, t=		90	Ci=	
1	**0.5**	1	1.0162			1.0358	**0.3409**
3.4	**2.2**	2	1.0096			0.8001	**0.2604**
5	**4.2**	3	1.0071			0.7836	**0.2552**
6.8	**5.9**	4	1.0045			0.684	**0.2208**
10	**8.4**	5	1.0013			0.433	**0.1326**
13.2	**11.6**	6	1.0116			0.2457	**0.0656**
16	**14.6**	7	1.0007			0.1085	**0.0177**
19.4	**17.7**	8	1.0108			0.0659	**0.0026**

Sample name: Ternary blend 1, 43% CEM I +7% LS + 50% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.55 7/4 S3 30/8 REPEAT			Exposure, t=	90	Ci=	
0.7	**0.35**	1	1.0045		1.286	**0.4332**
2.7	**1.7**	2	1.0056		0.7714	**0.2513**
5	**3.85**	3	1.0036		0.6945	**0.2247**
7.6	**6.3**	4	1.001		0.5607	**0.1779**
9.5	**8.55**	5	1.0032		0.4361	**0.1334**
12	**10.75**	6	1.0048		0.2315	**0.0610**
16	**14**	7	1.0103		0.1213	**0.0220**
19	**17.5**	8	1.0101		0.0792	**0.0073**
ZD 1.55 7/4 S1 23/6			Exposure, t=	89	Ci=	
1	**0.5**		1.0236		1.277	**0.4220**
3	**2**		1.0152		1.0481	**0.3456**
5	**4**		1.0176		0.7009	**0.2238**
7	**6**		1.0342		0.4655	**0.1395**
10	**8.5**		1.0432		0.2086	**0.0510**
13	**11.5**		1.0486		0.1721	**0.0384**
16	**14.5**		1.0045		0.0974	**0.0137**
20	**18**		1.0548		0.0914	**0.0111**
ZD 1.55 7/4 S2 23/6			Exposure, t=	89	Ci=	
1	**0.5**		1.0518		1.0942	**0.3491**
3	**2**		1.0225		0.8534	**0.2756**
5	**4**		1.09		0.6332	**0.1869**
7	**6**		1.0575		0.2996	**0.0808**
10	**8.5**		1.0868		0.116	**0.0188**
13	**11.5**		1.0938		0.0746	**0.0052**
16	**14.5**		1.0525		0.0589	**0.0001**
20	**18**		1.0222		0.0604	**0.0007**
ZD 1.55 7/4 S1 23/6			Exposure, t=	89	Ci=	
1	**0.5**		1.0413		1.236	**0.4009**
3	**2**		1.0048		0.9838	**0.3265**
5	**4**		1.0709		0.6542	**0.1972**
7	**6**		1.0789		0.306	**0.0813**
10	**8.5**		1.0523		0.1003	**0.0141**
13	**11.5**		1.0243		0.0634	**0.0017**
16	**14.5**		1.0735		0.058	**0.00**
20	**18**		1.0645		0.0603	**0.0006**

Sample name: Ternary blend 1, 43% CEM I +7% LS + 50% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.55 7/4 S1 XS 22/6			Exposure, t=	89	Ci=	
1	**0.5**		1.089		0.7622	**0.2291**
3	**2**		1.048		0.199	**0.0475**
5	**4**		1.0214		0.0815	**0.0080**
7	**6**		1.0869		0.0873	**0.0094**
10	**8.5**		1.0852		0.0587	**0.0001**
13	**11.5**		1.0294		0.0627	**0.0015**
16	**14.5**		1.0323		0.059	**0.0002**
20	**18**		1.061		0.0524	**0.00**
ZD 1.55 7/4 S2 XS 30/6			Exposure, t=	89	Ci=	
1	**0.5**		1.0793		1.1736	**0.3663**
3.3	**2.15**		1.02		0.2747	**0.0751**
5.5	**4.4**		1.0162		0.1166	**0.0203**
7	**6.25**		1.0131		0.0601	**0.0006**
10	**8.5**		1.0275		0.0731	**0.0050**
13.5	**11.75**		1.038		0.0623	**0.0013**
16	**14.75**		1.043		0.0583	**0.0001**
20	**18**		1.013		0.0649	**0.0022**
ZD 1.55 7/4 S3 XS 30/6			Exposure, t=	89	Ci=	
1	**0.5**		1.0508		1.0283	**0.3272**
2.7	**1.85**		1.065		0.2444	**0.0619**
5	**3.85**		1.0593		0.1329	**0.0249**
7	**6**		1.0239		0	**0.00**
10	**8.5**		1.068		0.0782	**0.0065**
13	**11.5**		1.048		0.0603	**0.0006**
16	**14.5**		1.0133		0.058	**0.00**
20	**18**		1.0186		0.06	**0.0005**

Sample name: CIIB-V, 70% CEM I + 30%FA

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZR1.5 29/4 S1 29/10			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0086		0.8776	0.2879
3	**2**	2	1.0028		1.1243	**0.3768**
5	**4**	3	1.0075		1.2408	**0.4160**
7	**6**	4	1.006		1.0486	**0.3489**
10	**8.5**	5	1.0022		1.0657	**0.3563**
13	**11.5**	6	1.0024		0.8074	**0.2649**
16	**14.5**	7	1.006		0.3518	**0.1034**
20	**18**	8	1.0069		0.3136	**0.0898**

Sample name: CIIB-V, 70% CEM I + 30%FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZR1.5 29/4 S1 8/11/10			Exposure, t=	96	Ci=	
1	**0.5**	1	1.0058		0.9972	**0.3309**
3	**2**	2	1.0037		1.092	**0.3650**
5	**4**	3	1.0067		1.1586	**0.3874**
7	**6**	4	1.0048		0.9686	**0.3211**
10	**8.5**	5	1.0084		0.8696	**0.2851**
13	**11.5**	6	1.0072		0.7359	**0.2384**
16	**14.5**	7	1.0017		0.5401	**0.1704**
20	**18**	8	1.0057		0.292	**0.0823**
ZR1.5 29/4 S2 8/11/10			Exposure, t=	96	Ci=	
1	**0.5**	1	1.0068		1.235	**0.4143**
3	**2**	2	1.0099		0.8194	**0.2671**
5	**4**	3	1.0031		1.2265	**0.4128**
7	**6**	4	1.0042		1.2467	**0.4195**
10	**8.5**	5	1.0045		1.1105	**0.3713**
13	**11.5**	6	1.0056		0.8315	**0.2725**
16	**14.5**	7	1.0025		0.5928	**0.1889**
20	**18**	8	1.003		0.4464	**0.1371**
ZR1.5 29/4 S1 21/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0067		0.9494	**0.3137**
3	**2**	2	1.0096		1.2118	**0.4050**
5	**4**	3	1.0025		1.1663	**0.3917**
7	**6**	4	1.0036		0.9562	**0.3171**
10	**8.5**	5	1.0062		0.7645	**0.2487**
13	**11.5**	6	1.0086		0.5818	**0.1839**
16	**14.5**	7	1.0054		0.3818	**0.1140**
20	**18**	8	1.0089		0.2111	**0.0536**
ZR1.5 29/4 S2 21/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0048		0.6284	**0.2011**
3	**2**	2	1.0082		0.9273	**0.3055**
5	**4**	3	1.0044		0.8675	**0.2855**
7	**6**	4	1.0066		0.7919	**0.2583**
10	**8.5**	5	1.004		0.503	**0.1570**
13	**11.5**	6	1.0055		0.4916	**0.1527**
16	**14.5**	7	1.009		0.4156	**0.1255**
20	**18**	8	1.0035		0.207	**0.0525**

Sample name: CIIB-V, 70% CEM I + 30%FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZR1.5 29/4 S3 21/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0053		0.8953	**0.2951**
3	**2**	2	1.0071		1.0886	**0.3626**
5	**4**	3	1.0044		1.0699	**0.3570**
7	**6**	4	1.0047		0.9299	**0.3075**
10	**8.5**	5	1.0034		0.6421	**0.2062**
13	**11.5**	6	1.0018		0.4214	**0.1284**
16	**14.5**	7	1.0034		0.2011	**0.0504**
20	**18**	8	1		0	**0.00**
ZR 1.5 29/4 S3 14/3			Exposure, t=	94	Ci=	
1	**0.5**	1	1.0336		0.9679	**0.3119**
3.5	**2.25**	2	1.0183		1.1426	**0.3774**
5.5	**4.5**	3	1.0288		1.091	**0.3558**
7.5	**6.5**	4	1.0609		0.8582	**0.2672**
10	**8.75**	5	1.0728		0.6304	**0.1890**
13	**11.5**	6	1.0146		0.3682	**0.1082**
16	**14.5**	7	1.0388		0.2342	**0.0600**
20	**18**	8	1.027		0.1351	**0.0264**

Sample name: CIIA-D, 92% CEM I + 8% SF

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 6/7 S1 26/5/11			Exposure, t=	108	Ci=	
1	**0.5**	1	1.0011		0.8229	**0.2707**
2	**1.5**	2	1.0052		1.2441	**0.4181**
3	**2.5**	3	1.0076		1.1926	**0.3990**
5	**4**	4	1.0072		0.843	**0.2761**
7	**6**	5	1.0066		0.6464	**0.2071**
9	**8**	6	1.0078		0.401	**0.1205**
12	**10.5**	7	1.005		0.2	**0.0499**
16	**14**	8	1.002		0.0681	**0.0034**
ZD1.4 6/7 S2 26/5/11			Exposure, t=	108	Ci=	
1	**0.5**	1	1.0015		0.8451	**0.2784**
2	**1.5**	2	1.0042		0.9254	**0.3060**
3	**2.5**	3	1.0039		0.9696	**0.3217**
5	**4**	4	1.0016		0.6916	**0.2241**
7	**6**	5	1.0083		0.4615	**0.1417**
9	**8**	6	1.0013		0.3225	**0.0935**
12	**10.5**	7	1.0027		0.173	**0.0405**
16	**14**	8	1.0081		0.0742	**0.0055**

Sample name: CIIA-D, 92% CEM I + 8% SF **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 6/7 S3 26/5/11			Exposure, t=	108	Ci=	
1	**0.5**	1	1.0011		0.957	**0.3182**
2	**1.5**	2	1.0023		1.3227	**0.4471**
3	**2.5**	3	1.0001		1.1322	**0.3806**
5	**4**	4	1.0045		0.9869	**0.3277**
7	**6**	5	1.0046		0.6544	**0.2103**
9	**8**	6	1.004		0.3732	**0.1111**
12	**10.5**	7	1.0017		0.2305	**0.0609**
16	**14**	8	1.0038		0.0858	**0.0097**
ZD1.4 6/7 S1 30/9			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0387		1.1178	**0.3615**
2	**1.5**	2	1.0279		1.0118	**0.3288**
3	**2.5**	3	1.0175		0.919	**0.2998**
5	**4**	4	1.0147		0.5132	**0.1589**
7	**6**	5	1.0133		0.3934	**0.1172**
9	**8**	6	1.0391		0.2512	**0.0657**
12	**10.5**	7	1.044		0.1264	**0.0231**
16	**14**	8	1.0209		0.062	**0.0012**
ZD1.4 6/7 S2 30/9			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0188		1.2308	**0.4079**
2	**1.5**	2	1.0422		1.0769	**0.3464**
3	**2.5**	3	1.0824		0.9768	**0.3008**
5	**4**	4	1.0129		0.649	**0.2067**
7	**6**	5	1.0737		0.3845	**0.1076**
9	**8**	6	1.0268		0.049	0.00
12	**10.5**	7	1.0598		0.1336	**0.0251**
16	**14**	8	1.0293		0.0698	**0.0039**
ZD1.4 6/7 S3 30/9			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0484		1.1859	**0.3812**
2	**1.5**	2	1.0501		1.1223	**0.3591**
3	**2.5**	3	1.069		1.0354	**0.3240**
5	**4**	4	1.097		0.8846	**0.2670**
7	**6**	5	1.0575		0.5117	**0.1519**
9	**8**	6	1.0608		0.2995	**0.0805**
12	**10.5**	7	1.0202		0.1723	**0.0396**
16	**14**	8	1.025		0.1196	**0.0211**

Sample name: Ternary blend 2, 46% CEM I + 46%ggbs + 8% SF

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.4 13/7 S1 1/6/11			Exposure, t=	114	Ci=	
1	**0.5**	1	1.0044		0.8503	**0.2795**
2	**1.5**	2	1.0039		0.6194	**0.1981**
3	**2.5**	3	1.002		0.472	**0.1463**
5	**4**	4	1.0003		0.2524	**0.0687**
7	**6**	5	1.0017		0.1599	**0.0359**
9	**8**	6	1.0004		0.0955	**0.0131**
12	**10.5**	7	1.0107		0.0728	**0.0050**
16	**14**	8	1.0186		0	**0.00**
ZS1.4 13/7 S2 1/6/11			Exposure, t=	114	Ci=	
1	**0.5**	1	1.0014		1.1012	**0.3691**
2	**1.5**	2	1.0074		0.887	**0.2916**
3	**2.5**	3	1.0103		0.6452	**0.2059**
5	**4**	4	1.0034		0.3916	**0.1177**
7	**6**	5	1.0167		0.1717	**0.0395**
9	**8**	6	1.0128		0.0812	**0.0080**
12	**10.5**	7	1.0127		0.0731	**0.0051**
16	**14**	8	1.0148		0.053	**0.00**
ZS1.4 13/7 S3 1/6/11			Exposure, t=	114	Ci=	
1	**0.5**	1	1.0092		0.8502	**0.2781**
2	**1.5**	2	1.0031		0.6463	**0.2077**
3	**2.5**	3	1.0044		0.5938	**0.1889**
5	**4**	4	1.0083		0.2374	**0.0629**
7	**6**	5	1.0008		0.1143	**0.0198**
9	**8**	6	1.0026		0.0759	**0.0062**
12	**10.5**	7	1.0051		0.0518	**0.00**
16	**14**	8	1.0141		0.0586	**0.0009**
ZS1.4 13/7 S1 29/9			Exposure, t=	92	Ci=	
1.7	**0.85**	1	1.0162		0.1891	**0.0456**
2	**1.85**	2	1.033		0.397	**0.1162**
3	**2.5**	3	1.07		0.2731	**0.0711**
5	**4**	4	1.0468		0.1668	**0.0367**
7	**6**	5	1.0768		0.0944	**0.0118**
9	**8**	6	1.0201		0.0551	**0.00**
12	**10.5**	7	1.0186		0.067	**0.0030**
16	**14**	8	1.0725		0.057	**0.00**

Sample name: Ternary blend 2, 46% CEM I + 46%ggbs + 8% SF **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.4 13/7 S2 29/9			Exposure, t=	92	Ci=	
1.5	**0.75**	1	1.0235		0.626	**0.1966**
2	**1.75**	2	1.0332		0.4446	**0.1325**
3	**2.5**	3	1.0765		0.2612	**0.0668**
5	**4**	4	1.0696		0.1462	**0.0291**
7	**6**	5	1.0275		0.0589	**0.0001**
9	**8**	6	1.0784		0.0782	**0.0065**
12	**10.5**	7	1.0774		0.0531	**0.00**
16	**14**	8	1.0578		0.0585	**0.0005**
ZS1.4 13/7 S3 29/9			Exposure, t=	92	Ci=	
1.2	**0.6**	1	1.0515		0.5775	**0.1750**
2	**1.6**	2	1.0892		0.3003	**0.0787**
3	**2.5**	3	1.091		0.2004	**0.0461**
5	**4**	4	1.0384		0.0511	**0.00**
7	**6**	5	1.022		0.0665	**0.0028**
9	**8**	6	1.0621		0.0606	**0.0007**
12	**10.5**	7	1.0717		0.0526	**0.00**
16	**14**	8	1.0865		0.0658	**0.0024**

Sample name: CIIA-LL, 85% CEM I + 15% LS Result

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 3/8 S1 23/3/11			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0089		1.0475	**0.3475**
2	**1.5**	2	1.0037		0.8557	**0.2816**
3	**2.5**	3	1.009		0.8	**0.2605**
5	**4**	4	1.0044		0.8051	**0.2635**
7	**6**	5	1.0091		0.678	**0.2176**
9	**8**	6	1.0044		0.5713	**0.1810**
12	**10.5**	7	1.0021		0.4285	**0.1309**
16	**14**	8	1.0052		0.3495	**0.1026**
ZD1.4 3/8 S2 23/3/11			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0011		1.0265	**0.3428**
2	**1.5**	2	1.0033		0.9199	**0.3044**
3	**2.5**	3	1.0095		0.8436	**0.2757**
5	**4**	4	1.0066		0.8163	**0.2669**
7	**6**	5	1.0061		0.746	**0.2423**
9	**8**	6	1.0036		0.6729	**0.2170**
12	**10.5**	7	1.0011		0.5234	**0.1646**
16	**14**	8	1.0028		0.3485	**0.1025**

Sample name: CIIA-LL, 85% CEM I + 15% LS | Result | **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 3/8 S3 23/3/11			Exposure, t=	91	Ci=	
1	**0.5**	1	1.002		1.0524	**0.3516**
2	**1.5**	2	1.0075		0.8258	**0.2700**
3	**2.5**	3	1.0044		0.7879	**0.2574**
5	**4**	4	1.0021		0.7335	**0.2388**
7	**6**	5	1.0071		0.6612	**0.2122**
9	**8**	6	1.0064		0.6204	**0.1979**
12	**10.5**	7	1.0025		0.5282	**0.1661**
16	**14**	8	1.0047		0.3255	**0.0942**
ZD1.4 3/8 S1 29/9			Exposure, t=	90	Ci=	
1	**0.5**	1	1.012		0.988	**0.3256**
2	**1.5**	2	1.0852		0.9137	**0.2794**
3	**2.5**	3	1.0573		0.9173	**0.2880**
5	**4**	4	1.0606		0.6371	**0.1934**
7	**6**	5	1.0406		0.691	**0.2155**
9	**8**	6	1.0276		0.5976	**0.1860**
12	**10.5**	7	1.0473		0.556	**0.1684**
16	**14**	8	1.027		0.3343	**0.0952**
ZD1.4 3/8 S2 29/9			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0785		1.153	**0.3598**
2	**1.5**	2	1.0458		0.9846	**0.3139**
3	**2.5**	3	1.0085		0.869	**0.2849**
5	**4**	4	1.0615		0.8356	**0.2595**
7	**6**	5	1.0588		0.7329	**0.2258**
9	**8**	6	1.0123		0.5304	**0.1653**
12	**10.5**	7	1.0546		0.4027	**0.1157**
16	**14**	8	1.0161		0.2768	**0.0762**
ZD1.4 3/8 S3 29/9			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0159		1.0828	**0.3574**
2.5	**1.75**	2	1.0434		0.9075	**0.2885**
3	**2.75**	3	1.0284		0.7738	**0.2466**
5	**4**	4	1.0471		0.9314	**0.2955**
7	**6**	5	1.0253		0.6493	**0.2043**
9	**8**	6	1.0634		0.5982	**0.1799**
12	**10.5**	7	1.0603		0.4015	**0.1147**
16	**14**	8	1.0527		0.2642	**0.0693**

Sample name: Ternary blend 3, 60% CEM I + 10% LS + 30% FA

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.5 9/8 S1 11/3/11			Exposure, t=	91	Ci=	
1	**0.5**	1	1.007		0.8242	**0.2696**
3	**2**	2	1.0067		0.8311	**0.2721**
5	**4**	3	1.0031		0.7356	**0.2393**
7	**6**	4	1.0032		0.3567	**0.1054**
10	**8.5**	5	1.0033		0.3451	**0.1013**
13	**11.5**	6	1.0087		0.242	**0.0645**
16	**14.5**	7	1.003		0.0854	**0.0095**
20	**18**	8	1.0043		0	**0.00**
ZS1.5 9/8 S2 11/3/11			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0049		0.7517	**0.2446**
3	**2**	2	1.0024		0.669	**0.2159**
5	**4**	3	1.0089		0.6599	**0.2113**
7	**6**	4	1.0091		0.5303	**0.1658**
10	**8.5**	5	1.0087		0.4713	**0.1451**
13	**11.5**	6	1.0026		0.3084	**0.0884**
16	**14.5**	7	1.0018		0.1687	**0.0390**
20	**18**	8	1.0088		0.0791	**0.0072**
ZS1.5 9/8 S3 11/3/11			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0037		0.694	**0.2245**
3	**2**	2	1.0059		0.7394	**0.2400**
5	**4**	3	1.0099		0.7819	**0.2539**
7	**6**	4	1.0084		0.5835	**0.1846**
10	**8.5**	5	1.0042		0.4503	**0.1383**
13	**11.5**	6	1.006		0.182	**0.0435**
16	**14.5**	7	1.0058		0.1251	**0.0235**
20	**18**	8	1.0067		0.0538	**0.00**
ZS1.5 9/8 S1 6/6/11			Exposure, t=	97	Ci=	
1	**0.5**	1	1.0091		0.8335	**0.2723**
3	**2**	2	1.0082		0.7427	**0.2406**
5	**4**	3	1.0085		0.6181	**0.1967**
7	**6**	4	1.0045		0.4755	**0.1472**
10	**8.5**	5	1.0086		0.1173	**0.0207**
13	**11.5**	6	1.0056		0.283	**0.0792**
16	**14.5**	7	1.0044		0.0734	**0.0053**
20	**18**	8	1.0068		0.0645	**0.0021**

Sample name: Ternary blend 3, 60% CEM I + 10% LS + 30% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.5 9/8 S2 6/6/11			Exposure, t=	97	Ci=	
1	**0.5**	1	1.0086		0.7357	**0.2380**
3	**2**	2	1.004		0.7779	**0.2540**
5	**4**	3	1.0083		0.548	**0.1721**
7	**6**	4	1.0078		0.4117	**0.1242**
10	**8.5**	5	1.0082		0.2641	**0.0723**
13	**11.5**	6	1.0045		0.1151	**0.0200**
16	**14.5**	7	1.0029		0.0858	**0.0097**
20	**18**	8	1.0015		0.0688	**0.0037**
ZS1.5 9/8 S3 6/6/11			Exposure, t=	97	Ci=	
1	**0.5**	1	1.0064		0.714	**0.2309**
3	**2**	2	1.009		0.7957	**0.2590**
5	**4**	3	1.0036		0.781	**0.2552**
7	**6**	4	1.0055		0.6599	**0.2120**
10	**8.5**	5	1.0057		0.454	**0.1394**
13	**11.5**	6	1.0041		0.281	**0.0786**
16	**14.5**	7	1.0083		0.2011	**0.0501**
20	**18**	8	1.0086		0.0842	**0.0090**
ZD 1.5 9/8 S1 3/10			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0582		0.8384	**0.2613**
3	**2**	2	0.9049		0.6605	**0.2359**
5	**4**	3	1.0491		0.7028	**0.2177**
7	**6**	4	1.0481		0.6527	**0.2010**
10	**8.5**	5	1.0752		0.4832	**0.1400**
13	**11.5**	6	1.0116		0.3218	**0.0923**
16	**14.5**	7	1.0572		0.2117	**0.0514**
20	**18**	8	1.0592		0.113	**0.0182**
ZD 1.5 9/8 S2 3/10			Exposure, t=	91	Ci=	
1.3	**0.65**	1	1.0362		0.9725	**0.3127**
3	**2.15**	2	1.0881		0.8962	**0.2729**
5	**4**	3	1.0412		0.8155	**0.2577**
7	**6**	4	1.0498		0.7676	**0.2395**
10	**8.5**	5	1.0576		0.457	**0.1336**
13	**11.5**	6	1.0572		0.255	**0.0659**
16	**14.5**	7	1.0405		0.0851	**0.0091**
20	**18**	8	1.0723		0.0572	**0.00**

Sample name: Ternary blend 3, 60% CEM I + 10% LS + 30% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams			V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.5 9/8 S3 3/10			Exposure, t=		91	Ci=	
1	**0.5**	1	1.0442			0.8737	**0.2768**
3	**2**	2	1.0728			0.9208	**0.2849**
5	**4**	3	1.0897			0.9608	**0.2935**
7	**6**	4	1.083			0.8587	**0.2619**
10	**8.5**	5	1.0364			0.6146	**0.1902**
13	**11.5**	6	1.0425			0.3739	**0.1073**
16	**14.5**	7	1.0934			0.2449	**0.0604**
20	**18**	8	1.0662			0.0997	**0.0137**

Sample name: CEM I, 100% CEM I

Depth	**MidPoint**	Layer	Mass, grams			V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.35 7/4 S1 30/8			Exposure, t=		90	Ci=	
0.5	**0.25**	1	1.0068	AV		1.2059	**0.4040**
2	**1.25**	2	1.0085	AW		1.123	**0.3742**
3.2	**2.6**	3	1.0065	AX		1.1194	**0.3737**
4.2	**3.7**	4	1.0098	AY		1.0414	**0.3451**
5.5	**4.85**	5	1.005	AZ		1.0125	**0.3365**
7.8	**6.65**	6	1.0016	BA		0.9474	**0.3146**
10.1	**8.95**	7	1.0075	BB		0.6085	**0.1935**
12	**11.05**	8	1.0088	BC		0.6188	**0.1969**
ZD1.35 7/4 S2 30/8			Exposure, t=		90	Ci=	
1	**0.5**	1	1.0073	BD		1.3226	**0.4449**
1.5	**1.25**	2	1.009	BE		1.1213	**0.3734**
2.3	**1.9**	3	1.001	BF		1.0721	**0.3590**
3.3	**2.8**	4	1.0015	BG		1.0068	**0.3357**
6	**4.65**	5	1.0097	BH		0.956	**0.3151**
8.3	**7.15**	6	1.0051	BI		0.8433	**0.2768**
10.3	**9.3**	7	1.0038	BJ		0.7513	**0.2447**
12	**11.15**	8	1	BK		0.5656	**0.1798**
ZD1.35 7/4 S3 30/8			Exposure, t=		90	Ci=	
1.2	**0.6**	1	1.0079	BL		1.3282	**0.4466**
2.2	**1.7**	2	1.0054	BM		0.9745	**0.3230**
3	**2.6**	3	1.0095	BN		0.9809	**0.3239**
4	**3.5**	4	1.0042	BO		0.9873	**0.3279**
6	**5**	5	1.0062	BP		0.8862	**0.2916**
8	**7**	6	1.01	BQ		0.6933	**0.2228**
10	**9**	7	1.001	BR		0.5251	**0.1653**
12	**11**	8	1.0045	BS		0.3831	**0.1146**

Sample name: CEM I, 100% CEM I **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 2.35 7/4 S1 24/6			Exposure, t=	89	Ci=	
1	**0.5**	1	1.0321		1.4616	**0.4819**
3	**2**	2	1.0157		1.2505	**0.4160**
5	**4**	3	1.0125		1.1355	**0.3771**
7	**6**	4	1.0028		1.0433	**0.3481**
10	**8.5**	5	1.0271		0.8765	**0.2823**
13	**11.5**	6	1.0059		0.6268	**0.2003**
16	**14.5**	7	1.007		0.4349	**0.1325**
20	**18**	8	1.0119		0.2825	**0.0785**
ZD 2.35 7/4 S2 24/6			Exposure, t=	89	Ci=	
1	**0.5**	1	1.088		1.5077	**0.4722**
3	**2**	2	1.023		1.2731	**0.4210**
5	**4**	3	1.0296		1.0817	**0.3524**
7	**6**	4	1.0185		0.9459	**0.3089**
10	**8.5**	5	1.091		0.7832	**0.2355**
13	**11.5**	6	1.0626		0.5669	**0.1697**
16	**14.5**	7	1.0254		0.3698	**0.1077**
20	**18**	8	1.0906		0.2677	**0.0681**
ZD 2.35 7/4 S3 24/6			Exposure, t=	89	Ci=	
1	**0.5**	1	1.0202		1.4882	**0.4969**
3	**2**	2	1.0529		1.313	**0.4224**
5	**4**	3	1.0261		1.0703	**0.3496**
7	**6**	4	1.0357		0.9154	**0.2934**
10	**8.5**	5	1.007		0.7123	**0.2302**
13	**11.5**	6	1.0335		0.5533	**0.1698**
16	**14.5**	7	1.0646		0.4387	**0.1267**
20	**18**	8	1.0007		0.2284	**0.0602**
ZD 1.35 7/4 S1 22/6 XS			Exposure, t=	112	Ci=	
1	**0.5**	1	1.098		0.8454	**0.2541**
2	**1.5**	2	1.0236		0.3398	**0.0975**
3	**2.5**	3	1.0318		0.2652	**0.0711**
5	**4**	4	1.0786		0.174	**0.0380**
7	**6**	5	1.0069		0.1508	**0.0326**
9	**8**	6	1.0354		0.1136	**0.0189**
12	**10.5**	7	1.0548		0.0862	**0.0094**
16	**14**	8	1.0827		0.0735	**0.0050**

Sample name: CEM I, 100% CEM I **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.35 7/4 S2 22/6 XS			Exposure, t=	112	Ci=	
1	**0.5**	1	1.018		1.1824	**0.3914**
2	**1.5**	2	1.0265		0.3076	**0.0861**
3	**2.5**	3	1.0721		0.2313	**0.0572**
5	**4**	4	1.0425		0.1733	**0.0391**
7	**6**	5	1.0244		0.118	**0.0206**
9	**8**	6	1.0403		0.0937	**0.0121**
12	**10.5**	7	1.0875		0.0875	**0.0095**
16	**14**	8	1.0153		0.077	**0.0065**
ZD 1.35 7/4 S3 22/6 XS			Exposure, t=	112	Ci=	
1	**0.5**	1	1.0491		0.5068	**0.1515**
2	**1.5**	2	1.0187		0.282	**0.0778**
3	**2.5**	3	1.0216		0.178	**0.0415**
5	**4**	4	1.0598		0.1951	**0.0457**
7	**6**	5	1.0672		0.1262	**0.0225**
9	**8**	6	1.0431		0.0971	**0.0132**
12	**10.5**	7	1.0608		0.0742	**0.0053**
16	**14**	8	1.0237		0.0708	**0.0043**

Sample name: CIVB-V, 50% CEM I + 50% FA

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.5 5/5 S1 8/11/10			Exposure, t=	90	Ci=	
1	**0.5**	1	1.003		0.9155	**0.3030**
3	**2**	2	1.0065		1.1648	**0.3897**
5	**4**	3	1.0086		1.0082	**0.3339**
7	**6**	4	1.0033		0.8608	**0.2835**
10	**8.5**	5	1.0017		0.7811	**0.2558**
13	**11.5**	6	1.0035		0.5357	**0.1686**
16	**14.5**	7	1.0044		0.4562	**0.1404**
20	**18**	8	1.0021		0.3287	**0.0956**
ZS1.5 5/5 S2 9/11/10			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0022		1.0982	**0.3678**
3	**2**	2	1.0075		0.8867	**0.2915**
5	**4**	3	1.0079		0.9591	**0.3168**
7	**6**	4	1.0056		0.8737	**0.2874**
10	**8.5**	5	1.0047		0.7159	**0.2320**
13	**11.5**	6	1.0084		0.5819	**0.1841**
16	**14.5**	7	1.0083		0.5909	**0.1872**
20	**18**	8	1.0017		0.5067	**0.1587**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.5 5/5 S2 9/11/10			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0018		1.0207	**0.3405**
3	**2**	2	1.0059		0.8626	**0.2834**
5	**4**	3	1.0045		0.9294	**0.3074**
7	**6**	4	1.0039		0.8124	**0.2663**
10	**8.5**	5	1.0071		0.6963	**0.2246**
13	**11.5**	6	1.0029		0.5411	**0.1706**
16	**14.5**	7	1.0079		0.4482	**0.1371**
20	**18**	8	1.0034		0.3188	**0.0920**
ZS1.5 5/5 S1 20/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0092		0.7078	**0.2281**
3	**2**	2	1.0022		0.8095	**0.2657**
5	**4**	3	1.0049		0.7242	**0.2349**
7	**6**	4	1.0023		0.5923	**0.1889**
10	**8.5**	5	1.0094		0.4748	**0.1463**
13	**11.5**	6	1.0037		0.3769	**0.1125**
16	**14.5**	7	1.0056		0.3197	**0.0921**
20	**18**	8	1.0032		0.155	**0.0342**
ZS1.5 5/5 S2 20/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0045		0.6455	**0.2072**
3	**2**	2	1.0071		0.7216	**0.2335**
5	**4**	3	1.0017		0.6283	**0.2017**
7	**6**	4	1.001		0.4299	**0.1316**
10	**8.5**	5	1.005		0.4183	**0.1270**
13	**11.5**	6	1.0029		0.3252	**0.0943**
16	**14.5**	7	1.0025		0.2701	**0.0749**
20	**18**	8	1.0079		0.1636	**0.0370**
ZS1.5 5/5 S3 20/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0058		0.541	**0.1701**
3	**2**	2	1.0074		0.5928	**0.1881**
5	**4**	3	1.0037		0.5703	**0.1808**
7	**6**	4	1.0067		0.4568	**0.1403**
10	**8.5**	5	1.0059		0.3756	**0.1118**
13	**11.5**	6	1.0022		0.2913	**0.0824**
16	**14.5**	7	1.0049		0.2211	**0.0574**
20	**18**	8	1.0038		0.1854	**0.0449**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.5 5/5 S1 22/3/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0263		0.5253	**0.1613**
3	**2**	2	1.0154		0.6642	**0.2115**
5.4	**4.2**	3	1.037		0.6724	**0.2099**
7.2	**6.3**	4	1.0224		0.4954	**0.1515**
10	**8.6**	5	1.0243		0.4984	**0.1523**
13	**11.5**	6	1.0279		0.3536	**0.1018**
16	**14.5**	7	1.0138		0.2555	**0.0689**
20	**18**	8	1.0135		0.1275	**0.0242**
ZS1.5 5/5 S2 22/3/11			Exposure, t=	90	Ci=	
1.3	**0.65**	1	1.0142		0.7123	**0.2286**
3.7	**2.5**	2	1.0194		0.6947	**0.2213**
5.5	**4.6**	3	1.0148		0.5772	**0.1813**
7	**6.25**	4	1.0705		0.5308	**0.1565**
10	**8.5**	5	1.017		0.4073	**0.1216**
13	**11.5**	6	1.0327		0.3074	**0.0855**
16	**14.5**	7	1.0129		0.2265	**0.0589**
20	**18**	8	1.0353		0.1223	**0.0219**
ZS1.5 5/5 S3 22/3/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0098		0.5926	**0.1876**
3	**2**	2	1.0591		0.5356	**0.1597**
5	**4**	3	1.0866		0.4874	**0.1400**
7	**6**	4	1.0496		0.4455	**0.1308**
10	**8.5**	5	1.028		0.3844	**0.1124**
13	**11.5**	6	1.0439		0.2669	**0.0708**
16	**14.5**	7	1.0872		0.2086	**0.0490**
20	**18**	8	1.0757		0.1318	**0.0242**
ZS2.5 5/5 S1 6/9			Exposure, t=	112	Ci=	
1	**0.5**	1	1.012		0.9991	**0.3295**
3	**2**	2	1.0178		0.6493	**0.2058**
5	**4**	3	1.0398		0.494	**0.1485**
7	**6**	4	1.0831		0.3772	**0.1044**
10	**8.5**	5	1.027		0.2703	**0.0732**
13	**11.5**	6	1.0804		0.1266	**0.0224**
16	**14.5**	7	1.004		0.0824	**0.0085**
20	**18**	8	1.0166		0.0544	**-0.0014**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS2.5 5/5 S2 6/9			Exposure, t=	112	Ci=	
1	**0.5**	1	1.0304		0.8301	**0.2655**
3	**2**	2	1.0675		0.5591	**0.1663**
5	**4**	3	1.0782		0.4393	**0.1253**
7	**6**	4	1.0354		0.12	**0.0211**
10	**8.5**	5	1.0245		0.2261	**0.0581**
13	**11.5**	6	1.0655		0.1644	**0.0353**
16	**14.5**	7	1.065		0.1112	**0.0176**
20	**18**	8	1.0129		0.0679	**0.0033**
ZS2.5 5/5 S3 6/9			Exposure, t=	112	Ci=	
1	**0.5**	1	1.0105		0.8816	**0.2888**
3	**2**	2	1.0732		0.5025	**0.1467**
5.5	**4.25**	3	1.0465		0.309	**0.0849**
7.5	**6.5**	4	1.0115		0.2611	**0.0711**
10	**8.75**	5	1.0377		0.1991	**0.0481**
13	**11.5**	6	1.024		0.1364	**0.0270**
16	**14.5**	7	1.0567		0.0792	**0.0070**
20	**18**	8	1.0076		0.067	**0.0030**

Sample name: CIIIB, 30% CEM I + 70% ggbs

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.5 6/5 S1 29/10			Exposure, t=	133	Ci=	
1	**0.5**	1	1.0095		0.7988	**0.2600**
3	**2**	2	1.004		0.6932	**0.2242**
5	**4**	3	1.0059		0.6367	**0.2038**
7	**6**	4	1.0066		0.491	**0.1524**
10	**8.5**	5	1.0073		0.3216	**0.0927**
13	**11.5**	6	1.0054		0.169	**0.0390**
16	**14.5**	7	1.0037		0.1451	**0.0306**
20	**18**	8	1.0008		0	**-0.0207**
ZS1.5 6/5 S2 10/11/10			Exposure, t=	145	Ci=	
1	**0.5**	1	1.0012		0.9216	**0.3057**
3	**2**	2	1.0065		0.8859	**0.2915**
5	**4**	3	1.0036		0.621	**0.1987**
7	**6**	4	1.0033		0.4747	**0.1471**
10	**8.5**	5	1.007		0.1966	**0.0487**
13	**11.5**	6	1.0022		0.0938	**0.0125**
16	**14.5**	7	1.0073		0.0679	**0.0034**
20	**18**	8	1.0084		0.0713	**0.0046**

Sample name: CIIIB, 30% CEM I + 70% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.5 6/5 S3 10/11/10			Exposure, t=	145	Ci=	
1	**0.5**	1	1.0044		1.0603	**0.3536**
3	**2**	2	1.0069		0.9653	**0.3193**
5	**4**	3	1.0006		0.7619	**0.2493**
7	**6**	4	1.0057		0.5686	**0.1799**
10	**8.5**	5	1.0045		0.2819	**0.0789**
13	**11.5**	6	1.0035		0.0933	**0.0124**
16	**14.5**	7	1.0078		0.0909	**0.0115**
20	**18**	8	1.003		0.056	**-0.0008**
ZS1.5 6/5 S1 21/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0021		0.5182	**0.1627**
3	**2**	2	1.0063		0.466	**0.1436**
5	**4**	3	1.0028		0.4513	**0.1389**
7	**6**	4	1.0051		0.3132	**0.0899**
10	**8.5**	5	1.0043		0.1474	**0.0314**
13	**11.5**	6	1.0062		0.0725	**0.0050**
16	**14.5**	7	1.0075		0.0573	**-0.0004**
20	**18**	8	1.0029		0.0673	**0.0032**
ZS1.5 6/5 S2 21/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0049		0.8791	**0.2895**
3	**2**	2	1.0055		0.7852	**0.2563**
5	**4**	3	1.0066		0.5703	**0.1803**
7	**6**	4	1.0018		0.405	**0.1227**
10	**8.5**	5	1.0046		0.0927	**0.0121**
13	**11.5**	6	1.0043		0.0678	**0.0033**
16	**14.5**	7	1.0071		0	**-0.0205**
20	**18**	8	1.0041		0.0594	**0.0004**
ZS1.5 6/5 S3 21/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0075		0.9118	**0.3003**
3	**2**	2	1.0019		0.9025	**0.2987**
5	**4**	3	1.0064		0.6517	**0.2090**
7	**6**	4	1.0011		0.394	**0.1189**
10	**8.5**	5	1.0029		0.1678	**0.0387**
13	**11.5**	6	1.0042		0.0806	**0.0079**
16	**14.5**	7	1.002		0.0688	**0.0037**
20	**18**	8	1.0039		0.0577	**-0.0002**

Sample name: CIIIB, 30% CEM I + 70% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.5 6/5 S1 11/3/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0056		1.077	**0.3591**
3	**2**	2	1.005		0.9052	**0.2987**
5	**4**	3	1.0089		0.5775	**0.1824**
7	**6**	4	1.0037		0.174	**0.0409**
10	**8.5**	5	1.0078		0.062	**0.0013**
13	**11.5**	6	1.0095		0.0564	**-0.0007**
16	**14.5**	7	1.0052		0.0582	**0.0000**
20	**18**	8	1.0078		0.0574	**-0.0003**
ZS1.5 6/5 S2 11/3/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0028		0.9069	**0.3000**
3	**2**	2	1.0052		0.7845	**0.2561**
5	**4**	3	1.0053		0.5748	**0.1821**
7	**6**	4	1.0099		0.354	**0.1038**
10	**8.5**	5	1.0045		0.1944	**0.0480**
13	**11.5**	6	1.0042		0.0803	**0.0078**
16	**14.5**	7	1.0027		0.0567	**-0.0006**
20	**18**	8	1.0034		0.0591	**0.0003**
ZS1.5 6/5 S3 11/3/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.008		0.936	**0.3087**
3	**2**	2	1.0047		0.7694	**0.2509**
5	**4**	3	1.0099		0.5386	**0.1686**
7	**6**	4	1.0015		0.3	**0.0855**
10	**8.5**	5	1.0077		0.0909	**0.0115**
13	**11.5**	6	1.0089		0.0616	**0.0011**
16	**14.5**	7	1.0053		0.0574	**-0.0003**
20	**18**	8	1.0038		0.0672	**0.0031**
ZS1.5 6/5 S1 6/9			Exposure, t=	112	Ci=	
1	**0.5**	1	1.0741		1.1161	**0.3491**
3	**2**	2	1.0944		0.8191	**0.2464**
5	**4**	3	1.0498		0.5159	**0.1545**
7	**6**	4	1.0185		0.1967	**0.0482**
10	**8.5**	5	1.0356		0.1051	**0.0160**
13	**11.5**	6	1.0625		0.053	**-0.0018**
16	**14.5**	7	1.0326		0.054	**-0.0015**
20	**18**	8	1.0896		0.064	**0.0018**

Sample name: CIIIB, 30% CEM I + 70% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.5 6/5 S2 6/9			Exposure, t=	112	Ci=	
1.2	**0.6**	1	1.0955		1.048	**0.3203**
3	**2.1**	2	1.0673		0.6883	**0.2092**
5	**4**	3	1.0403		0.3345	**0.0941**
7.5	**6.25**	4	1.0221		0.1753	**0.0406**
10	**8.75**	5	1.0341		0.0927	**0.0118**
13	**11.5**	6	1.0104		0.064	**0.0020**
16	**14.5**	7	1.0124		0.05	**-0.0029**
20	**18**	8	1.0752		0.054	**-0.0014**
ZS1.5 6/5 S3 6/9			Exposure, t=	112	Ci=	
1	**0.5**	1	1.0095		1.1571	**0.3858**
3	**2**	2	1.0688		0.93	**0.2891**
5	**4**	3	1.0143		0.5023	**0.1552**
7	**6**	4	1.0804		0.1503	**0.0302**
10	**8.5**	5	1.0124		0.0875	**0.0102**
13	**11.5**	6	1.0221		0.0771	**0.0065**
16	**14.5**	7	1.0277		0.0558	**-0.0009**
20	**18**	8	1.0623		0.0676	**0.0031**

Sample name: CIIA-LL, 85% CEM I + 15% LS

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.35 2/6 S1 11/11/10			Exposure, t=	99	Ci=	
1	**0.5**	1	1.0083		1.0041	**0.3325**
2	**1.5**	2	1.0055		0.9394	**0.3106**
3	**2.5**	3	1.0029		0.9313	**0.3086**
5	**4**	4	1.0034		0.77	**0.2514**
7	**6**	5	1.0037		0.6925	**0.2240**
9	**8**	6	1.0038		0.545	**0.1719**
12	**10.5**	7	1.002		0.4686	**0.1451**
16	**14**	8	1.006		0.3206	**0.0924**
ZS1.35 2/6 S2 11/11/10			Exposure, t=	99	Ci=	
1	**0.5**	1	1.0025		0.9639	**0.3202**
2	**1.5**	2	1.0073		0.8801	**0.2892**
3	**2.5**	3	1.0031		0.7754	**0.2534**
5	**4**	4	1.0053		0.6254	**0.2000**
7	**6**	5	1.0093		0.6382	**0.2037**
9	**8**	6	1.005		0.4616	**0.1422**
12	**10.5**	7	1.0062		0.4905	**0.1523**
16	**14**	8	1.004		0.4012	**0.1211**

Sample name: CIIA-LL, 85% CEM I + 15% LS **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.35 2/6 S3 11/11/10			Exposure, t=	99	Ci=	
1	**0.5**	1	1.0018		0.8417	**0.2772**
2	**1.5**	2	1.0026		0.76	**0.2481**
3	**2.5**	3	1.0091		0.7389	**0.2391**
5	**4**	4	1.0088		0.6307	**0.2011**
7	**6**	5	1.0044		0.5706	**0.1808**
9	**8**	6	1.0036		0.5055	**0.1580**
12	**10.5**	7	1.0039		0.4549	**0.1400**
16	**14**	8	1.0035		0.347	**0.1020**
ZS1.35 2/6 S1 24/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0092		0.9809	**0.3241**
2	**1.5**	2	1.0023		0.7174	**0.2331**
3	**2.5**	3	1.008		0.6665	**0.2139**
5	**4**	4	1.0024		0.5727	**0.1819**
7	**6**	5	1.0076		0.5361	**0.1681**
9	**8**	6	1.0055		0.4845	**0.1502**
12	**10.5**	7	1.0093		0.4022	**0.1208**
16	**14**	8	1.0022		0.3124	**0.0899**
ZS1.35 2/6 S2 24/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0018		1.2425	**0.4190**
2	**1.5**	2	1.0037		1.1482	**0.3849**
3	**2.5**	3	1.0081		0.932	**0.3072**
5	**4**	4	1.0046		0.8351	**0.2741**
7	**6**	5	1.0082		0.6972	**0.2246**
9	**8**	6	1.0083		0.6303	**0.2011**
12	**10.5**	7	1.009		0.5066	**0.1575**
16	**14**	8	1.0018		0.3389	**0.0993**
ZS1.35 2/6 S3 24/1/11			Exposure, t=	90	Ci=	
1	**0.5**	1	1.008		0.9507	**0.3138**
2	**1.5**	2	1.0037		0.7703	**0.2515**
3	**2.5**	3	1.0046		0.7486	**0.2436**
5	**4**	4	1.0038		0.6651	**0.2143**
7	**6**	5	1.0048		0.6074	**0.1937**
9	**8**	6	1.0098		0.6087	**0.1932**
12	**10.5**	7	1.0046		0.4034	**0.1218**
16	**14**	8	1.0086		0.331	**0.0958**

Sample name: CIIA-LL, 85% CEM I + 15% LS **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.35 2/6 S1 3/6/11			Exposure, t=	116	Ci=	
1	**0.5**	1	1.0026		1.014	**0.3379**
3	**2**	2	1.0078		0.9433	**0.3113**
5	**4**	3	1.0046		0.7933	**0.2594**
7	**6**	4	1.0056		0.663	**0.2132**
10	**8.5**	5	1.0044		0.5865	**0.1864**
13	**11.5**	6	1.0054		0.4062	**0.1227**
16	**14.5**	7	1.0064		0.3048	**0.0868**
20	**18**	8	1.005		0.1938	**0.0478**
ZS1.35 2/6 S2 3/6/11			Exposure, t=	116	Ci=	
1	**0.5**	1	1.0065		0.9757	**0.3231**
2	**1.5**	2	1.0088		0.7527	**0.2440**
3	**2.5**	3	1.0055		0.6949	**0.2244**
5	**4**	4	1.0067		0.6366	**0.2036**
7	**6**	5	1.0031		0.5225	**0.1640**
9	**8**	6	1.0054		0.4447	**0.1362**
12	**10.5**	7	1.0044		0.3268	**0.0948**
16	**14**	8	1.0027		0.1932	**0.0477**
ZS1.35 2/6 S3 3/6/11			Exposure, t=	116	Ci=	
1	**0.5**	1	1.0076		1.1037	**0.3678**
2	**1.5**	2	1.0078		0.8992	**0.2958**
3	**2.5**	3	1.0032		0.6916	**0.2238**
5	**4**	4	1.0051		0.38	**0.1135**
7	**6**	5	1.0044		0.5459	**0.1721**
9	**8**	6	1.0081		0.4409	**0.1345**
12	**10.5**	7	1.0084		0.3499	**0.1025**
16	**14**	8	1.0056		0.2207	**0.0572**
ZS1.35 2/6 S1 6/9			Exposure, t=	112	Ci=	
1	**0.5**	1	1.0256		1.1557	**0.3793**
2	**1.5**	2	1.0096		1.0274	**0.3403**
3	**2.5**	3	1.0322		0.9589	**0.3093**
5	**4**	4	1.0262		0.761	**0.2427**
7	**6**	5	1.0875		0.8112	**0.2454**
9	**8**	6	1.0323		0.6217	**0.1935**
12	**10.5**	7	1.0384		0.4645	**0.1387**
16	**14**	8	1.0227		0.2967	**0.0826**
20	**18**	9	1.0279		0.2014	**0.0493**

Sample name: CIIA-LL, 85% CEM I + 15% LS **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.35 2/6 S2 6/9			Exposure, t=	112	Ci=	
1	**0.5**	1	1.0096		0.9755	**0.3220**
2	**1.5**	2	1.016		0.8124	**0.2631**
3	**2.5**	3	1.0469		0.8232	**0.2590**
5	**4**	4	1.0016		0.622	**0.1995**
7	**6**	5	1.0361		0.6483	**0.2019**
9	**8**	6	1.0474		0.5952	**0.1817**
12	**10.5**	7	1.065		0.471	**0.1374**
16	**14**	8	1.0224		0.2528	**0.0674**
20	**18**	9	1.07677		0.1741	**0.0381**
ZS1.35 2/6 S3 6/9			Exposure, t=	112	Ci=	
1	**0.5**	1	1.054		0.9325	**0.2940**
2	**1.5**	2	1.0779		0.8491	**0.2601**
3	**2.5**	3	1.0443		0.799	**0.2514**
5	**4**	4	1.0118		0.6842	**0.2193**
7	**6**	5	1.0396		0.5767	**0.1768**
9	**8**	6	1.0106		0.4337	**0.1317**
12	**10.5**	7	1.0463		0.3566	**0.1011**
16	**14**	8	1.0231		0.2693	**0.0731**
20	**18**	9	1.0263		0.1954	**0.0473**

Sample name: CIIA-D, 92% CEM I + 8% SF

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.35 15/7 S1 2/6			Exposure, t=	115	Ci=	
1	**0.5**	1	1.0661		1.048	**0.3291**
3	**2**	2	1.0437		0.6836	**0.2124**
5	**4**	3	1.0069		0.5568	**0.1755**
7	**6**	4	1.0236		0.293	**0.0813**
10	**8.5**	5	1.0629		0.137	**0.0262**
13	**11.5**	6	1.0154		0.1001	**0.0146**
16	**14.5**	7	1.0249		0.0659	**0.0026**
20	**18**	8	1.0662		0.0815	**0.0077**
ZS1.35 15/7 S2 2/6			Exposure, t=	115	Ci=	
1	**0.5**	1	1.0924		1.1562	**0.3563**
3	**2**	2	1.0314		0.8788	**0.2820**
5	**4**	3	1.0198		0.6052	**0.1901**
7	**6**	4	1.015		0.3668	**0.1077**
10	**8.5**	5	1.0368		0.1245	**0.0226**
13	**11.5**	6	1.0808		0.0834	**0.0082**
16	**14.5**	7	1.072		0.0918	**0.0111**
20	**18**	8	1.0547		0.0834	**0.0084**

Sample name: CIIA-D, 92% CEM I + 8% SF **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.35 15/7 S3 2/6			Exposure, t=	115	Ci=	
1	**0.5**	1	1.045		0.9697	**0.3092**
3	**2**	2	1.0069		0.7424	**0.2408**
5	**4**	3	1.0523		0.5386	**0.1618**
7	**6**	4	1.0122		0.3427	**0.0996**
10	**8.5**	5	1.0292		0.1394	**0.0279**
13	**11.5**	6	1.0318		0.1461	**0.0302**
16	**14.5**	7	1.0266		0.0995	**0.0142**
20	**18**	8	1.0823		0.0739	**0.0051**
ZS1.35 15/7 S1 30/9			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0264		0.9041	**0.2921**
2	**1.5**	2	1.012		0.7551	**0.2441**
3	**2.5**	3	1.0516		0.6592	**0.2026**
4	**3.5**	4	1.0289		0.13	**0.0247**
6	**5**	5	1.0206		0.233	**0.0607**
8	**7**	6	1.0608		0.1181	**0.0200**
10	**9**	7	1.0413		0.0853	**0.0092**
12	**11**	8	1.0827		0.0713	**0.0042**
ZS1.35 15/7 S2 30/9			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0917		1.0379	**0.3181**
2	**1.5**	2	1.0114		0.8841	**0.2894**
3	**2.5**	3	1.0266		0.7656	**0.2442**
5	**4**	4	1.0134		0.558	**0.1748**
7	**6**	5	1.0854		0.2468	**0.0616**
9	**8**	6	1.0406		0.1075	**0.0167**
12	**10.5**	7	1.0205		0.0601	**0.0006**
16	**14**	8	1.06		0.0644	**0.0020**
ZS1.35 15/7 S3 30/9			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0442		0.9476	**0.3019**
2	**1.5**	2	1.011		0.8414	**0.2746**
3	**2.5**	3	1.0427		0.7543	**0.2366**
5	**4**	4	1.0637		0.5839	**0.1752**
7	**6**	5	1.0261		0.3306	**0.0941**
9	**8**	6	1.0528		0.2006	**0.0479**
12	**10.5**	7	1.0457		0.1231	**0.0220**
16	**14**	8	1.0765		0.083	**0.0081**

Sample name: CIIIB, 30% CEM I + 70% ggbs

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 5/8A S1 23/3/11			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0331		0.8274	**0.1583**
2	**1.5**	2	1.0567		0.7214	**0.1335**
3	**2.5**	3	1.0817		0.6045	**0.1074**
5	**4**	4	1.0512		0.4384	**0.0769**
7	**6**	5	1.0622		0.3057	**0.0495**
9	**8**	6	1.0886		0.2045	**0.0286**
12	**10.5**	7	1.033		0.178	**0.0246**
16	**14**	8	1.0337		0.1801	**0.0251**
ZD1.4 5/8A S2 23/3/11			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0808			**-0.0115**
2	**1.5**	2	1.0927		0.8612	**0.1563**
3	**2.5**	3	1.0446		0.6887	**0.1284**
5	**4**	4	1.0281		0.5376	**0.0992**
7	**6**	5	1.0704		0.3001	**0.0480**
9	**8**	6	1.0428		0.1673	**0.0222**
12	**10.5**	7	1.0861		0.0857	**0.0054**
16	**14**	8	1.0565		0.06	**0.0003**
ZD1.4 5/8A S3 23/3/11			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0092		0.6688	**0.1287**
2	**1.5**	2	1.0574		0.6358	**0.1162**
3	**2.5**	3	1.0729		0.6682	**0.1209**
5	**4**	4	1.0733		0.4729	**0.0822**
7	**6**	5	1.0446		0.291	**0.0474**
9	**8**	6	1.0413		0.1172	**0.0120**
12	**10.5**	7	1.0405		0.094	**0.0073**
16	**14**	8	1.0483		0.0569	**-0.0003**
ZD1.4 5/8A S1 9/6/11			Exposure, t=	98	Ci=	
1	**0.5**	1	1.162		0.992	**0.1709**
2	**1.5**	2	1.0631		0.9132	**0.1710**
3	**2.5**	3	1.084		0.7528	**0.1363**
5	**4**	4	1.133		0.4405	**0.0717**
7	**6**	5	1.1222		0.1706	**0.0213**
9	**8**	6	1.1969		0.093	**0.0062**
12	**10.5**	7	1.0201		0.0649	**0.0014**
16	**14**	8	1.0184		0.0497	**-0.0018**

Sample name: CIIIB, 30% CEM I + 70% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 5/8A S2 10/6			Exposure, t=	99	Ci=	
1	**0.5**	1	1.0033		0.7589	**0.1485**
2	**1.5**	2	1.0115		0.7093	**0.1369**
3	**2.5**	3	1.09		0.6343	**0.1124**
5	**4**	4	1.0695		0.4504	**0.0780**
7	**6**	5	1.0391		0.155	**0.0198**
9	**8**	6	1.0718		0.1364	**0.0155**
12	**10.5**	7	1.0221		0.078	**0.0041**
16	**14**	8	1.0281		0.0817	**0.0048**
ZD1.4 5/8A S3 10/6			Exposure, t=	99	Ci=	
1	**0.5**	1	1.0664		0.8967	**0.1672**
2	**1.5**	2	1.0187		0.8519	**0.1657**
3	**2.5**	3	1.0643		0.767	**0.1416**
5	**4**	4	1.0652		0.3831	**0.0648**
7	**6**	5	1.0397		0.1669	**0.0222**
9	**8**	6	1.0215		0.0983	**0.0083**
12	**10.5**	7	1.0201		0.0717	**0.0028**
16	**14**	8	1.011		0.069	**0.0022**
ZD 1.4 5/8A S1 3/10			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0789			
2.2	**1.6**	2	1.0588		0.8356	**0.1561**
3	**2.6**	3	1.0543		0.7579	**0.1411**
5	**4**	4	1.043		0.5313	**0.0965**
7	**6**	5	1.0313		0.2516	**0.0399**
9	**8**	6	1.0816		0.1472	**0.0175**
12	**10.5**	7	1.0833		0.1002	**0.0082**
16	**14**	8	1.0768		0.0796	**0.0042**
ZD 1.4 5/8A S2 3/10			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0136		1.0593	**0.2100**
2	**1.5**	2	1.0473		0.9656	**0.1843**
3	**2.5**	3	1.0919		0.7159	**0.1281**
5	**4**	4	1.0955		0.2533	**0.0379**
7	**6**	5	1.074		0.1412	**0.0164**
9	**8**	6	1.0832		0.056	**-0.0005**
12	**10.5**	7	1.0531		0.0632	**0.0010**
16	**14**	8	1.0169		0.049	**-0.0020**

Sample name: CIIIB, 30% CEM I + 70% ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.4 5/8A S3 3/10			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0416		0.8919	**0.1702**
2	**1.5**	2	1.0223		0.6997	**0.1334**
3	**2.5**	3	1.0348		0.5819	**0.1076**
5	**4**	4	1.0626		0.334	**0.0552**
7	**6**	5	1.025		0.1382	**0.0166**
9	**8**	6	1.0462		0.127	**0.0140**
12	**10.5**	7	1.0933		0.0949	**0.0071**
16	**14**	8	1.0372		0.052	**-0.0013**

Sample name: CIVB-V, 50% CEM I + 50% FA

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS1.4 5/8B S1 14/3/11			Exposure, t=	94	Ci=	
1	**0.5**	1	1.0019		0.6926	**0.2244**
1.7	**1.35**	2	1.0038		0.6186	**0.1979**
2.7	**2.2**	3	1.0016		0.6907	**0.2238**
5	**3.85**	4	1.0057		0.6481	**0.2079**
7	**6**	5	1.0081		0.5222	**0.1631**
9	**8**	6	1.0014		0.4022	**0.1217**
12	**10.5**	7	1.002		0.3251	**0.0944**
16	**14**	8	1.0099		0.2389	**0.0634**
ZS1.4 5/8B S1 14/3/11			Exposure, t=	94	Ci=	
1	**0.5**	1	1.0043		0.5109	**0.1597**
2	**1.5**	2	1.0074		0.4696	**0.1447**
3	**2.5**	3	1.0039		0.6098	**0.1947**
5	**4**	4	1.0054		0.6397	**0.2050**
7	**6**	5	1.0092		0.5571	**0.1752**
9	**8**	6	1.006		0.4824	**0.1494**
12	**10.5**	7	1.0081		0.403	**0.1212**
16	**14**	8	1.0087		0.2702	**0.0745**
ZS1.4 5/8B S1 14/3/11			Exposure, t=	94	Ci=	
1	**0.5**	1	1.0018		0.4337	**0.1328**
2	**1.5**	2	1.0046		0.4135	**0.1253**
3	**2.5**	3	1.0054		0.4485	**0.1376**
5	**4**	4	1.0054		0.453	**0.1392**
7	**6**	5	1.0048		0.4029	**0.1216**
9	**8**	6	1.002		0.3629	**0.1078**
12	**10.5**	7	1.0061		0.3429	**0.1003**
16	**14**	8	1.0043		0.3104	**0.0890**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZS 2.4 5/8B S1 9/6/11			Exposure, t=	98	Ci=	
1	**0.5**	1	1.1728		0.9763	**0.2775**
2	**1.5**	2	1.0648		0.7054	**0.2154**
3	**2.5**	3	1.0329		0.6406	**0.1998**
5	**4**	4	1.1921		0.6638	**0.1801**
7	**6**	5	1.1239		0.5083	**0.1419**
9	**8**	6	1.1323		0.4031	**0.1079**
12	**10.5**	7	1.0528		0.2777	**0.0739**
16	**14**	8	1.1628		0.162	**0.0316**
ZS 2.4 5/8B S2 9/6/11			Exposure, t=	98	Ci=	
1	**0.5**	1	1.0025		0.7164	**0.2327**
2	**1.5**	2	1.1946		0.7892	**0.2169**
3	**2.5**	3	1.0532		0.6512	**0.1996**
5	**4**	4	1.0291		0.5985	**0.1861**
7	**6**	5	1.00303		0.5379	**0.1695**
9	**8**	6	1.0258		0.454	**0.1367**
12	**10.5**	7	1.1356		0.4176	**0.1122**
16	**14**	8	1.1931		0.3154	**0.0764**
ZS 2.4 5/8B S3 9/6/11			Exposure, t=	98	Ci=	
1	**0.5**	1	1.0633		0.7834	**0.2417**
2	**1.5**	2	1.0766		0.7677	**0.2336**
3	**2.5**	3	1.0606		0.6776	**0.2070**
5	**4**	4	1.0918		0.5435	**0.1575**
7	**6**	5	1.0801		0.4811	**0.1388**
9	**8**	6	1.0917		0.4003	**0.1110**
12	**10.5**	7	1.0556		0.3268	**0.0902**
16	**14**	8	1.13		0.2615	**0.0637**
Z D 2.4 5/8B S1 4/10			Exposure, t=	92	Ci=	
1	**0.5**	1	1.0124		0.6678	**0.2134**
2	**1.5**	2	1.0358		0.5363	**0.1636**
3	**2.5**	3	1.0171		0.5299	**0.1644**
5	**4**	4	1.0438		0.2953	**0.0805**
7	**6**	5	1.0386		0.2907	**0.0793**
9	**8**	6	1.0313		0.2327	**0.0599**
12	**10.5**	7	1.0876		0.164	**0.0344**
16	**14**	8	1.029		0.0789	**0.0071**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
Z D 2.4 5/8B S2 4/10			Exposure, t=	92	Ci=	
1	**0.5**	1	1.0387		0.7063	**0.2211**
2	**1.5**	2	1.0241		0.5595	**0.1735**
3	**2.5**	3	1.0131		0.5106	**0.1583**
5	**4**	4	1.0974		0.4231	**0.1178**
7	**6**	5	1.0845		0.3476	**0.0946**
9	**8**	6	1.063		0.2617	**0.0678**
12	**10.5**	7	1.0207		0.2135	**0.0539**
16	**14**	8	1.077		0.1605	**0.0336**
Z D 2.4 5/8B S3 4/10			Exposure, t=	92	Ci=	
1	**0.5**	1	1.0451		0.7699	**0.2414**
2	**1.5**	2	1.072		0.6532	**0.1967**
3	**2.5**	3	1.0192		0.5797	**0.1813**
5	**4**	4	1.041		0.515	**0.1555**
7	**6**	5	1.0256		0.4185	**0.1245**
9	**8**	6	1.0401		0.3324	**0.0934**
12	**10.5**	7	1.0424		0.2384	**0.0612**
16	**14**	8	1.0601		0.098	**0.0133**

Sample name: CIVB-V, 50% CEM I + 50% FA

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 5/8C S1 8/6/11			Exposure, t=	97	Ci=	
1	**0.5**	1	1.008		0.5234	**0.1636**
2	**1.5**	2	1.0058		0.6098	**0.1944**
3	**2.5**	3	1.0078		0.619	**0.1972**
5	**4**	4	1.0039		0.5362	**0.1687**
7	**6**	5	1.0055		0.4437	**0.1359**
9	**8**	6	1.0045		0.3803	**0.1136**
12	**10.5**	7	1.0027		0.2804	**0.0785**
16	**14**	8	1.0045		0.1859	**0.0450**
ZD1.4 5/8C S2 8/6/11			Exposure, t=	97	Ci=	
1	**0.5**	1	1.0099		0.6523	**0.2085**
2	**1.5**	2	1.007		0.5831	**0.1847**
3	**2.5**	3	1.0088		0.5719	**0.1805**
5	**4**	4	1.0022		0.4647	**0.1437**
7	**6**	5	1.0067		0.4884	**0.1514**
9	**8**	6	1.0093		0.4067	**0.1224**
12	**10.5**	7	1.003		0.302	**0.0861**
16	**14**	8	1.0025		0.2048	**0.0518**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.4 5/8C S3 8/6/11			Exposure, t=	97	Ci=	
1	**0.5**	1	1.0092		0.5802	**0.1833**
2	**1.5**	2	1.0058		0.5894	**0.1872**
3	**2.5**	3	1.0071		0.5552	**0.1749**
5	**4**	4	1.0068		0.4626	**0.1423**
7	**6**	5	1.0043		0.4447	**0.1364**
9	**8**	6	1.0026		0.3829	**0.1148**
12	**10.5**	7	1.0079		0.2988	**0.0846**
16	**14**	8	1.0058		0.2212	**0.0574**
ZD1.4 5/8C S1 8/6 repeat			Exposure, t=	97	Ci=	
1	**0.5**	1	1.0781		0.5841	**0.1729**
2	**1.5**	2	1.0412		0.6476	**0.2006**
3	**2.5**	3	1.0135		0.6413	**0.2039**
5	**4**	4	1.0877		0.5954	**0.1750**
7	**6**	5	1.0684		0.4721	**0.1373**
9	**8**	6	1.0377		0.371	**0.1068**
12	**10.5**	7	1.0384		0.2927	**0.0800**
16	**14**	8	1.0149		0.1937	**0.0473**
ZD1.4 5/8C S2 8/6/11 repeat			Exposure, t=	97	Ci=	
1	**0.5**	1	1.0465		0.6868	**0.2129**
2	**1.5**	2	1.0538		0.6147	**0.1872**
3	**2.5**	3	1.0556		0.6116	**0.1858**
5	**4**	4	1.0608		0.5686	**0.1705**
7	**6**	5	1.0543		0.4969	**0.1475**
9	**8**	6	1.0123		0.4202	**0.1267**
12	**10.5**	7	1.0533		0.298	**0.0807**
16	**14**	8	1.04		0.2157	**0.0536**
ZD1.4 5/8C S3 8/6/11 repeat			Exposure, t=	97	Ci=	
1	**0.5**	1	1.0508		0.5974	**0.1819**
2	**1.5**	2	1.0438		0.6067	**0.1862**
3	**2.5**	3	1.0749		0.6013	**0.1791**
5	**4**	4	1.07		0.0782	**0.0066**
7	**6**	5	1.0541		0.4944	**0.1467**
9	**8**	6	1.01		0.3823	**0.1137**
12	**10.5**	7	1.0674		0.3348	**0.0918**
16	**14**	8	1.0111		0.2142	**0.0546**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.4 5/8C S1 22/3			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0852		0.7283	**0.2189**
2	**1.5**	2	1.0817		0.6161	**0.1828**
3	**2.5**	3	1.0413		0.7135	**0.2230**
5	**4**	4	1.0601		0.7305	**0.2248**
7	**6**	5	1.0103		0.5565	**0.1748**
9	**8**	6	1.0965		0.5302	**0.1526**
12	**10.5**	7	1.0236		0.3732	**0.1090**
16	**14**	8	1.026		0.2091	**0.0521**
ZD 1.4 5/8C S2 22/3			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0325		0.6121	**0.1901**
2	**1.5**	2	1.0509		0.4903	**0.1457**
3	**2.5**	3	1.0348		0.5889	**0.1818**
5	**4**	4	1.0417		0.5536	**0.1685**
7	**6**	5	1.04		0.4777	**0.1429**
9	**8**	6	1.01		0.429	**0.1301**
12	**10.5**	7	1.01		0.3377	**0.0981**
16	**14**	8	1.0497		0.2433	**0.0625**
ZD 1.4 5/8C S3 22/3			Exposure, t=	90	Ci=	
1	**0.5**	1	1.0176		0.589	**0.1849**
2	**1.5**	2	1.0695		0.514	**0.1510**
2.7	**2.35**	3	1.0561		0.5379	**0.1610**
5	**3.85**	4	1.0601		0.5056	**0.1496**
7	**6**	5	1.0901		0.4452	**0.1258**
9	**8**	6	1.0203		0.3334	**0.0956**
12	**10.5**	7	1.0357		0.3499	**0.0998**
16	**14**	8	1.0476		0.2425	**0.0623**
ZD 1.4 5/8C S1 3/10			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0727		0.786	**0.2405**
2	**1.5**	2	1.0358		0.5838	**0.1798**
3	**2.5**	3	1.0461		0.5604	**0.1701**
5	**4**	4	1.0388		0.4865	**0.1461**
7	**6**	5	1.0901		0.4074	**0.1135**
9	**8**	6	1.0686		0.2903	**0.0770**
12	**10.5**	7	1.0619		0.2201	**0.0540**
16	**14**	8	1.023		0.1344	**0.0264**

Sample name: CIVB-V, 50% CEM I + 50% FA **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.4 5/8C S2 3/10			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0426		0.7729	**0.2430**
2	**1.5**	2	1.0714		0.557	**0.1650**
3	**2.5**	3	1.0321		0.4841	**0.1462**
5	**4**	4	1.0968		0.5002	**0.1428**
7	**6**	5	1.026		0.3786	**0.1107**
9	**8**	6	1.0326		0.2458	**0.0644**
12	**10.5**	7	1.0391		0.1751	**0.0398**
16	**14**	8	1.0278		0.0809	**0.0078**
ZD 1.4 5/8C S3 3/10			Exposure, t=	91	Ci=	
1	**0.5**	1	1.0371		0.772	**0.2439**
2	**1.5**	2	1.042		0.5405	**0.1640**
3	**2.5**	3	1.0255		0.5047	**0.1543**
5	**4**	4	1.018		0.229	**0.0594**
7	**6**	5	1.0527		0.3247	**0.0897**
9	**8**	6	1.0693		0.2367	**0.0591**
12	**10.5**	7	1.0231		0.1599	**0.0352**
16	**14**	8	1.09		0.0677	**0.0030**

Sample name: CIIIA, 50% CEM I + 50%ggbs

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.45 9/8 S1 14/3/11			Exposure, t=	94	Ci=	
1	**0.5**	1	1.0018		1.1312	**0.3796**
3	**2**	2	1.0099		1.3239	**0.4442**
5	**4**	3	1.0032		0.7755	**0.2534**
7	**6**	4	1.005		0.4765	**0.1475**
10	**8.5**	5	1.0031		0.1388	**0.0284**
12.5	**11.25**	6	1.0093		0.0645	**0.0022**
16	**14.25**	7	1.0066		0	**-0.0205**
20	**18**	8	1.0058		0.066	**0.0027**
ZD1.45 9/8 S2 14/3/11			Exposure, t=	94	Ci=	
1	**0.5**	1	1.0082		1.1065	**0.3686**
3	**2**	2	1.0021		1.1326	**0.3800**
5	**4**	3	1.0084		0.9181	**0.3022**
7	**6**	4	1.0071		0.5854	**0.1855**
10	**8.5**	5	1.0068		0.276	**0.0766**
13	**11.5**	6	1.0027		0.093	**0.0123**
16	**14.5**	7	1.0094		0.0656	**0.0026**
20	**18**	8	1.0057		0.0606	**0.0008**

Sample name: CIIIA, 50% CEM I + 50%ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD1.45 9/8 S3 14/3/11			Exposure, t=	94	Ci=	
1	**0.5**	1	1.0035		1.1422	**0.3829**
3	**2**	2	1.0013		0.9988	**0.3330**
5	**4**	3	1.0035		0.7408	**0.2411**
7	**6**	4	1.004		0.4731	**0.1464**
10	**8.5**	5	1.0032		0.2625	**0.0721**
13	**11.5**	6	1.0094		0.1063	**0.0168**
16	**14.5**	7	1.0055		0.0611	**0.0010**
20	**18**	8	1.0035		0.0644	**0.0021**
ZD1.45 9/8 S1 23/6/11			Exposure, t=	89	Ci=	
1	**0.5**	1	1.0231		1.18	**0.3887**
3	**2**	2	1.0036		1.0557	**0.3523**
5	**4**	3	1.0585		0.7603	**0.2351**
7	**6**	4	1.0056		0.3857	**0.1154**
10	**8.5**	5	1.074		0.1548	**0.0318**
13	**11.5**	6	1.0199		0.1026	**0.0154**
16	**14.5**	7	1.068		0.077	**0.0062**
20	**18**	8	1.0829		0.0635	**0.0017**
ZD1.45 9/8 S2 23/6/11			Exposure, t=	89	Ci=	
1	**0.5**	1	1.0505		1.2071	**0.3877**
3	**2**	2	1.022		1.1065	**0.3636**
5	**4**	3	1.0063		0.7297	**0.2365**
7	**6**	4	1.0494		0.4824	**0.1433**
10	**8.5**	5	1.0226		0.1894	**0.0454**
13	**11.5**	6	1.0104		0.1064	**0.0169**
16	**14.5**	7	1.0615		0.0838	**0.0085**
20	**18**	8	1.0644		0.0812	**0.0076**
ZD1.45 9/8 S3 23/6/11			Exposure, t=	89	Ci=	
1	**0.5**	1	1.009		1.3052	**0.4381**
3	**2**	2	1.022		1.178	**0.3884**
5	**4**	3	1.013		0.7971	**0.2585**
7	**6**	4	1.0929		0.51	**0.1465**
10	**8.5**	5	1.0561		0.152	**0.0314**
13	**11.5**	6	1.0289		0.0812	**0.0079**
16	**14.5**	7	1.072		0.0621	**0.0012**
20	**18**	8	1.0127		0.0595	**0.0004**

Sample name: CIIIA, 50% CEM I + 50%ggbs **Cont'd…**

Depth	**MidPoint**	Layer	Mass, grams		V_3 AgCl, ml	**CC (% by mass of concrete)**
ZD 1.45 9/8 S1 4/10			Exposure, t=	92	Ci=	
1.5	**0.75**	1	1.0553		1.1976	**0.3827**
3.2	**2.35**	2	1.0896		1.1866	**0.3671**
5	**4.1**	3	1.0548		0.7931	**0.2469**
7	**6**	4	1.0969		0.507	**0.1450**
10	**8.5**	5	1.038		0.3007	**0.0828**
13	**11.5**	6	1.0384		0.1318	**0.0251**
16	**14.5**	7	1.0258		0.0662	**0.0027**
20	**18**	8	1.0101		0	**-0.0205**
ZD 1.45 9/8 S2 4/10			Exposure, t=	92	Ci=	
1	**0.5**	1	1.0571		1.3868	**0.4455**
3	**2**	2	1.0409		1.3012	**0.4233**
5	**4**	3	1.023		0.9801	**0.3194**
7	**6**	4	1.0677		0.6346	**0.1913**
10	**8.5**	5	1.0346		0.3598	**0.1033**
13	**11.5**	6	1.0744		0.2069	**0.0490**
16	**14.5**	7	1.0604		0.0964	**0.0127**
20	**18**	8	1.0162		0.0501	**-0.0029**
ZD 1.45 9/8 S3 4/10			Exposure, t=	92	Ci=	
1	**0.5**	1	1.0713		1.5165	**0.4825**
3	**2**	2	1.0096		1.2908	**0.4328**
5	**4**	3	1.0367		0.8277	**0.2631**
7	**6**	4	1.0461		0.5218	**0.1571**
10	**8.5**	5	1.0884		0.2538	**0.0637**
13	**11.5**	6	1.0628		0.1086	**0.0168**
16	**14.5**	7	1.0107		0.0866	**0.0099**
20	**18**	8	1.0353		0.0868	**0.0097**

APPENDIX F

Raw data for NT Build 492

Specimen	test date	init temp, °C	new init Ω, mA	voltage applied, V	final Ω, mA	final temp, °C	test duration	ave LXd	D_{nssm}, m^2/s
ZD 2.4 2/3 A	24/08/2010	24.5	0.05	30	0.05	21.9	24	0.050	1.0210E-11
		24.5	0.05	30	0.05	21.9	24	0.050	9.7434E-12
ZD 2.4 2/3 B		24.4	0.05	30	0.06	21.7	24	0.050	6.6085E-12
		24.4	0.05	30	0.06	21.7	24	0.050	7.0526E-12
ZD 2.5 6/4 A	25/08/2010	24.4	0.03	40	0.04	21.5	24	0.050	4.3969E-12
		24.4	0.03	40	0.04	21.5	24	0.050	3.8495E-12
ZD 2.5 6/4 B		24.4	0.03	40	0.04	21.3	24	0.050	4.1664E-12
		24.4	0.03	40	0.04	21.3	24	0.050	4.6817E-12
ZD 2.4 26/1 A	30/08/2010	23.7	0.06	20	0.06	22.2	24	0.050	1.4727E-11
		23.7	0.06	20	0.06	22.2	24	0.050	1.2706E-11
ZD 2.4 26/1 B		23.7	0.08	20	0.07	22.2	24	0.050	1.7168E-11
		23.7	0.08	20	0.07	22.2	24	0.050	1.7264E-11
ZS 1.5 5/5 A	31/08/2010	23.7	0.06	25	0.11	24.6	24	0.050	6.6862E-12
		23.7	0.06	25	0.11	24.6	24	0.050	7.8498E-12
ZS 1.5 5/5 B		23.7	0.07	25	0.12	23.9	24	0.050	6.8651E-12
		23.7	0.07	25	0.12	23.9	24	0.050	6.4900E-12
ZD 1.4 6/7 A	01/09/2010	24.8	0.03	35	0.04	21.5	24	0.050	5.7485E-12
		24.8	0.03	35	0.04	21.5	24	0.050	5.9118E-12
ZD 1.4 6/7 B		24.8	0.03	35	0.04	21.6	24	0.050	5.8457E-12
		24.8	0.03	35	0.04	21.6	24	0.050	5.3327E-12
ZD 1.35 7/4 A	02/09/2010	24.7	0.06	20	0.05	21.3	24	0.050	1.2607E-11
		24.7	0.06	20	0.05	21.3	24	0.050	1.2175E-11
ZD 1.35 7/4 B		24.8	0.06	20	0.05	21.3	24	0.050	1.5597E-11
		24.8	0.06	20	0.05	21.3	24	0.050	1.4308E-11
ZS 1.5 6/5 A	06/09/2010	22.7	0.03	50	0.03	21.7	24	0.050	3.6886E-12
		22.7	0.03	50	0.03	21.7	24	0.050	3.9655E-12
ZS 1.5 6/5 B		22.7	0.03	60	0.03	21.8	24	0.050	3.6609E-12
		22.7	0.03	60	0.03	21.8	24	0.050	3.5728E-12
ZD 2.5 6/4 A	07/09/2010	23.8	0.03	40	0.03	21.4	24	0.050	4.8282E-12
		23.8	0.03	40	0.03	21.4	24	0.050	4.6084E-12
ZD 2.5 6/4 B		23.8	0.03	40	0.03	21.6	24	0.050	5.3423E-12
		23.8	0.03	40	0.03	21.6	24	0.050	6.5112E-12
ZD 2.55 25/2 A	08/09/2010	24.1	0.03	60	0.04	22.3	24	0.050	2.2701E-12
		24.1	0.03	60	0.04	22.3	24	0.050	2.4445E-12
		24.1	0.03	60	0.05	22.3	24	0.050	3.2649E-12
		24.1	0.03	60	0.05	22.3	24	0.050	2.8928E-12

Cont'd…

Specimen	test date	init temp, °C	new init Ω, mA	voltage applied, V	final Ω, mA	final temp, °C	test duration	ave LXd	D_{nssm}, m²/s
ZS 1.35 15/7 A	14/09/2010	23.5	0.03	60	0.03	21.7	24	0.050	3.0756E-12
		23.5	0.03	60	0.03	21.7	24	0.050	2.9114E-12
ZR 1.5 29/4 A	15/09/2010	24.1	0.06	25	0.09	21.9	24	0.050	1.9462E-11
		24.1	0.06	25	0.09	21.9	24	0.050	1.9532E-11
ZR 1.5 29/4 B		24	0.06	25	0.09	21.9	24	0.050	2.0079E-11
		24	0.06	25	0.09	21.9	24	0.050	2.1246E-11
ZD 1.55 7/4 A	16/09/2010	24.2	0.03	50	0.03	21.5	24	0.050	2.4130E-12
		24.2	0.03	50	0.03	21.5	24	0.050	2.3150E-12
ZD 1.55 7/4 B		24.2	0.03	50	0.03	21.5	24	0.050	4.1590E-12
		24.2	0.03	50	0.03	21.5	24	0.050	4.1690E-12
ZS 2.35 2/6 A	21/09/2010	24	0.07	25	0.07	21.6	24	0.050	1.9251E-11
		24	0.07	25	0.07	21.6	24	0.050	1.9995E-11
ZS 2.35 2/6 B		24	0.07	25	0.08	21.7	24	0.050	1.8038E-11
		24	0.07	25	0.08	21.7	24	0.050	1.8338E-11
ZS 1.4 13/7 A	22/09/2010	23.7	0.02	60	0.03	21.7	24	0.050	1.5057E-12
		23.7	0.02	60	0.03	21.7	24	0.050	1.7068E-12
ZS 1.4 13/7 B		23.7	0.02	60	0.03	21.7	24	0.050	2.1627E-12
		23.7	0.02	60	0.03	21.7	24	0.050	1.8363E-12
ZD 1.4 6/7 A	20/10/2010	23.4	0.03	40	0.04	21.4	24	0.050	3.0533E-12
		23.4	0.03	40	0.04	21.4	24	0.050	3.5226E-12
ZD 1.4 6/7 B		23.3	0.03	40	0.03	21	24	0.050	2.9258E-12
		23.3	0.03	40	0.03	21	24	0.050	3.1972E-12
ZS 1.4 13/7 A	21/10/2010	23.4	0.02	60	0.04	21.4	24	0.050	1.9792E-12
		23.4	0.02	60	0.04	21.4	24	0.050	2.0027E-12
ZS 1.4 13/7 B		23.3	0.02	60	0.03	21	24	0.050	1.9420E-12
		23.3	0.02	60	0.03	21	24	0.050	2.0249E-12
ZD 1.55 18/2 A	26/10/2010	23.2	0.04	30	0.06	21.8	24	0.050	2.0948E-11
		23.2	0.04	30	0.06	21.8	24	0.050	2.2180E-11
ZD 1.55 18/2 B		23.2	0.04	30	0.06	21.8	24	0.050	2.2935E-11
		23.2	0.04	30	0.06	21.8	24	0.050	2.2872E-11
ZD 1.35 7/4 A	16/12/2010	21.4	0.06	25	0.07	22.4	24	0.050	1.2157E-11
		21.4	0.06	25	0.07	22.4	24	0.050	1.1634E-11
ZD 1.35 7/4 B		21.4	0.06	25	0.06	22	24	0.050	1.1144E-11
		21.4	0.06	25	0.06	22	24	0.050	1.1117E-11

Cont'd…

Specimen	test date	init temp, °C	new init Ω, mA	voltage applied, V	final Ω, mA	final temp, °C	test duration	ave LXd	D_{nssm}, m²/s
ZD 1.5 6/4 A	20/12/2010	22.8	0.03	50	0.04	22.2	24	0.050	4.1349E-12
		22.8	0.03	50	0.04	22.2	24	0.050	3.8325E-12
ZD 1.5 6/4 B		22.8	0.03	50	0.35	21.9	24	0.050	3.2530E-12
		22.8	0.03	50	0.35	21.9	24	0.050	3.5514E-12
ZS 1.5 6/5 A	21/12/2010	23.8	0.02	60	0.04	22.5	48	0.050	1.5987E-12
		23.8	0.02	60	0.04	22.5	48	0.050	1.9623E-12
ZS 1.5 6/5 B		23.8	0.02	60	0.03	22.1	48	0.050	1.7857E-12
		23.8	0.02	60	0.03	22.1	48	0.050	1.9937E-12
ZS 2.35 2/6 A	23/12/2010	22.8	0.06	25	0.07	22.5	24	0.050	1.6250E-11
		22.8	0.06	25	0.07	22.5	24	0.050	1.7838E-11
ZS 2.35 2/6 B		22.1	0.06	25	0.07	22	24	0.050	1.6364E-11
		22.1	0.06	25	0.07	22	24	0.050	1.6339E-11
ZD 1.4 3/8 A	06/01/2011	22.9	0.05	25	0.06	22	24	0.050	1.6180E-11
		22.9	0.05	25	0.06	22	24	0.050	1.6169E-11
ZD 1.4 3/8 B		22.8	0.05	25	0.06	22	24	0.050	1.4764E-11
		22.8	0.05	25	0.06	22	24	0.050	1.4956E-11
ZS 1.5 5/5 A	05/01/2011	23.6	0.04	40	0.21	25.6	24	0.050	1.4748E-11
		23.6	0.04	40	0.21	25.6	24	0.050	1.4576E-11
ZS 1.5 5/5 B		23.5	0.04	40	0.19	24.1	24	0.050	1.8189E-11
		23.5	0.04	40	0.19	24.1	24	0.050	1.8189E-11
ZD1.4 5/8C A	11/01/2011	25.7	0.03	35	0.09	22.8	24	0.050	2.0867E-11
		25.7	0.03	35	0.09	22.8	24	0.050	2.0867E-11
ZD1.4 5/8C B		25.5	0.03	35	0.07	22.4	24	0.050	1.5865E-11
		25.5	0.03	35	0.07	22.4	24	0.050	1.5687E-11
ZD1.4 5/8B A	12/01/2011	22.7	0.04	30	0.09	22.2	24	0.050	2.3816E-11
		22.7	0.04	30	0.09	22.2	24	0.050	2.2005E-11
ZD1.4 5/8B B		22.6	0.04	30	0.08	22.4	24	0.050	1.7300E-11
		22.6	0.04	30	0.08	22.4	24	0.050	1.6882E-11
ZD1.4 5/8A A	13/01/2011	23	0.02	60	0.03	22	24	0.050	1.9044E-12
		23	0.02	60	0.03	22	24	0.050	1.7714E-12
ZD1.4 5/8A B		22.9	0.02	60	0.02	22.3	24	0.050	3.7598E-12
		22.9	0.02	60	0.02	22.3	24	0.050	3.4313E-12

Cont'd…

Specimen	test date	init temp, °C	new init Ω, mA	voltage applied, V	final Ω, mA	final temp, °C	test duration	ave LXd	D_{nssm}, m²/s
ZS1.5 9/8 A	17/01/2011	23.6	0.03	40	0.06	22.1	24	0.050	6.5805E-12
		23.6	0.03	40	0.06	22.1	24	0.050	6.6740E-12
ZS1.5 9/8 B		23.8	0.03	40	0.06	22.4	24	0.050	8.3231E-12
		23.8	0.03	40	0.06	22.4	24	0.050	8.1704E-12
ZS1.5 9/8 D	18/01/2011	23.9	0.04	40	0.07	22.4	24	0.050	7.2567E-12
		23.9	0.04	40	0.07	22.4	24	0.050	7.6257E-12
ZD1.45 9/8 A	27/01/2011	25	0.03	35	0.03	21.9	24	0.050	3.1608E-12
		25	0.03	35	0.03	21.9	24	0.050	3.2018E-12
ZD1.45 9/8 B		24.8	0.03	35	0.03	21.9	24	0.050	4.7243E-12
		24.8	0.03	35	0.03	21.9	24	0.050	4.6471E-12
ZD1.4 6/7 A	31/01/2011	21.8	0.03	40	0.03	22	24	0.051	3.4979E-12
		21.8	0.03	40	0.03	22	24	0.051	3.7589E-12
ZD1.4 6/7 B		21.9	0.02	40	0.03	22.2	24	0.050	4.5084E-12
		21.9	0.02	40	0.03	22.2	24	0.050	5.3418E-12
ZS1.4 13/7 A	01/02/2011	23.5	0.01	60	0.02	22.2	96	0.050	1.3179E-12
		23.5	0.01	60	0.02	22.2	96	0.050	1.3057E-12
ZS1.4 13/7 B		23.5	0.01	60	0.02	22.2	96	0.050	9.7874E-13
		23.5	0.01	60	0.02	22.2	96	0.050	1.0399E-12
ZS1.35 15/7 A	07/02/2011	22.3	0.02	60	0.02	22.1	24	0.050	1.6416E-12
		22.3	0.02	60	0.02	22.1	24	0.050	1.8133E-12
ZS1.35 15/7 B		22.3	0.02	60	0.02	22.4	24	0.050	2.0023E-12
		22.3	0.02	60	0.02	22.4	24	0.050	2.3037E-12
ZD1.5 5/5 A	14/02/2011	24.5	0.03	40	0.09	23	24	0.048	7.5237E-12
		24.5	0.03	40	0.09	23	24	0.048	8.8143E-12
ZD1.5 5/5 B		24.5	0.02	40	0.08	23.1	24	0.048	1.0988E-11
		24.5	0.02	40	0.08	23.1	24	0.048	9.2798E-12
ZD1.4 5/8C A	15/02/2011	24.7	0.04	40	0.05	21.8	24	0.051	1.2153E-11
		24.7	0.04	40	0.05	21.8	24	0.051	1.1692E-11
ZD1.4 5/8C B		24.7	0.03	40	0.04	21.8	24	0.050	1.1817E-11
		24.7	0.03	40	0.04	21.8	24	0.050	1.1178E-11
ZD1.4 5/8B A	16/02/2011	26.3	0.04	35	0.05	22	24	0.048	1.5889E-11
		26.3	0.04	35	0.05	22	24	0.048	1.6260E-11
ZD1.4 5/8B B		26.3	0.04	35	0.05	22.1	24	0.050	1.2728E-11
		26.3	0.04	35	0.05	22.1	24	0.050	1.2580E-11

Cont'd…

Specimen	test date	init temp, °C	new init Ω, mA	voltage applied, V	final Ω, mA	final temp, °C	test duration	ave LXd	D_{nssm}, m²/s
ZD2.55 18.2 A	08/03/2011	22.7	0.02	60	0.05	21.4	48	0.050	1.8496E-12
		22.7	0.02	60	0.05	21.4	48	0.050	1.9364E-12
ZD2.55 18.2 B		23	0.02	60	0.03	21	48	0.051	2.3662E-12
		23	0.02	60	0.03	21	48	0.051	1.9239E-12
ZD1.55 24/2	21/03/2011	25.9	0.02	60	0.08	21.8	48	0.048	9.1043E-13
		25.9	0.02	60	0.08	21.8	48	0.048	8.2083E-13
ZD1.5 9/8 A	14/04/2011	23.2	0.03	50	0.04	20.4	24	0.050	4.8583E-12
		23.2	0.03	50	0.04	20.4	24	0.050	4.8475E-12
ZD1.5 9/8 B		23.1	0.03	50	0.03	20	24	0.051	4.2085E-12
		23.1	0.03	50	0.03	20	24	0.051	4.5691E-12
ZD1.4 26/1 A	19/04/2011	24	0.07	20	0.06	20.2	24	0.050	1.5669E-11
		24	0.07	20	0.06	20.2	24	0.050	1.5399E-11
ZD1.4 26/1 B		24	0.07	20	0.06	20.1	24	0.047	1.5014E-11
		24	0.07	20	0.06	20.1	24	0.047	1.4148E-11
ZD1.55 7/4 A	21/04/2011	24.1	0.02	60	0.03	21.7	48	0.050	1.6328E-12
		24.1	0.02	60	0.03	21.7	48	0.050	1.6682E-12
ZD1.55 7/4 B		24.1	0.02	60	0.03	20.1	48	0.050	2.4369E-12
		24.1	0.02	60	0.03	20.1	48	0.050	2.5925E-12
ZD1.35 7/4 A	25/04/2011	23	0.06	20	0.06	20	24	0.050	1.5309E-11
		23	0.06	20	0.06	20	24	0.050	1.9922E-11
ZD1.35 7/4 B		23	0.06	25	0.06	20	24	0.051	1.2246E-11
		23	0.06	25	0.06	20	24	0.051	1.2930E-11
ZD1.5 6/4 A	26/04/2011	22.1	0.03	60	0.03	20.4	24	0.050	2.8975E-12
		22.1	0.03	60	0.03	20.4	24	0.050	2.5001E-12
ZD1.5 6/4 B		22.1	0.03	60	0.04	20.2	24	0.051	2.5575E-12
		22.1	0.03	60	0.04	20.2	24	0.051	2.4442E-12
ZD1.4 3/8 A	04/05/2011	23.7	0.06	30	0.06	20.7	24	0.050	1.4442E-11
		23.7	0.06	30	0.06	20.7	24	0.050	1.4601E-11
ZD1.4 3/8 B		25.2	0.06	30	0.06	20	24	0.051	1.3782E-11
		25.2	0.06	30	0.06	20	24	0.051	1.3542E-11
ZD1.4 5/8C A	05/05/2011	23.5	0.03	50	0.04	20.3	24	0.050	7.6127E-12
		23.5	0.03	50	0.04	20.3	24	0.050	7.1244E-12
ZD1.4 5/8C A		23.5	0.03	50	0.04	20.3	24	0.050	6.8832E-12
		23.5	0.03	50	0.04	20.3	24	0.050	6.4574E-12

Cont'd…

Specimen	test date	init temp, °C	new init Ω, mA	voltage applied, V	final Ω, mA	final temp, °C	test duration	ave LXd	D_{nssm}, m²/s
ZD1.45 9/8 A	09/05/2011	23	0.03	50	0.03	20.2	24	0.049	4.6177E-12
		23	0.03	50	0.03	20.2	24	0.049	4.3900E-12
ZD1.45 9/8 B		23	0.03	50	0.03	20.1	24	0.050	7.6209E-12
		23	0.03	50	0.03	20.1	24	0.050	7.7562E-12
ZS1.4 5/8B A	10/05/2011	23.1	0.03	50	0.04	20.5	24	0.051	8.8642E-12
		23.1	0.03	50	0.04	20.5	24	0.051	8.3919E-12
ZS1.4 5/8B B		23.1	0.03	50	0.04	20.5	24	0.051	7.7406E-12
		23.1	0.03	50	0.04	20.5	24	0.051	7.5106E-12
ZD1.4 5/8A A	11/05/2011	23.5	0.02	60	0.035	21	48	0.051	2.8466E-12
		23.5	0.02	60	0.035	21	48	0.051	3.5274E-12
		23.5	0.02	60	0.03	20.4	48	0.051	2.1416E-12
		23.5	0.02	60	0.03	20.4	48	0.051	2.1628E-12
ZS2.35 2/6 A	08/11/2011	23.9	0.06	30	0.08	21.5	24	0.051	1.6221E-11
		23.9	0.06	30	0.08	21.5	24	0.051	1.6408E-11
ZS2.35 2/6 B		23.4	0.06	30	0.08	20.7	24	0.051	2.2024E-11
		23.4	0.06	30	0.08	20.7	24	0.051	2.2853E-11
ZS1.35 15/7 A	09/11/2011	23.4	0.02	60	0.025	20.6	24	0.051	2.3578E-12
		23.4	0.02	60	0.025	20.6	24	0.051	1.9496E-12
ZS1.35 15/7 B		23.2	0.02	60	0.025	20.4	24	0.051	4.5858E-12
		23.2	0.02	60	0.025	20.4	24	0.051	3.2158E-12
ZD1.45 5/8C A	14/11/2011	22.8	0.01	60	0.04	22.1	96	0.050	2.3465E-12
		22.8	0.01	60	0.04	22.1	96	0.050	2.3412E-12
ZD1.45 5/8C B		22.6	0.01	60	0.04	22.7	96	0.051	2.1411E-12
		22.6	0.01	60	0.04	22.7	96	0.051	2.4710E-12
ZD1.4 6/7 A	21/11/2011	23.9	0.03	40	0.04	20.5	24	0.050	3.3383E-12
		23.9	0.03	40	0.04	20.5	24	0.050	3.4584E-12
ZD1.4 6/7 B		23.8	0.03	40	0.05	21.3	24	0.050	3.9361E-12
		23.8	0.03	40	0.05	21.3	24	0.050	4.6247E-12
ZR2.5 29/4 A	21/11/2011	23.2	0.03	40	0.04	20.8	24	0.051	5.9384E-12
		23.2	0.03	40	0.04	20.8	24	0.051	6.0227E-12
ZR2.5 29/4 B		23.7	0.03	40	0.03	20.6	24	0.051	6.0194E-12
		23.7	0.03	40	0.03	20.6	24	0.051	5.9171E-12

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Specimen	test date	init temp, °C	new init Ω, mA	voltage applied, V	final Ω, mA	final temp, °C	test duration	ave LXd	D_{nssm}, m²/s
ZS1.5 9/8 A	28/11/2011	22.1	0.02	60	0.03	21.2	24	0.051	2.8683E-12
		22.1	0.02	60	0.03	21.2	24	0.051	3.2614E-12
ZS1.5 9/8 B		22.1	0.02	60	0.03	20.9	24	0.050	3.3264E-12
		22.1	0.02	60	0.03	20.9	24	0.050	3.0771E-12
ZD1.4 3/8 A	28/11/2011	22.1	0.05	30	0.06	20.6	24	0.050	1.3784E-11
		22.1	0.05	30	0.06	20.6	24	0.050	1.2883E-11
ZD1.4 3/8 B		22.1	0.05	30	0.06	20.8	24	0.050	1.4371E-11
		22.1	0.05	30	0.06	20.8	24	0.050	1.3903E-11
ZS1.5 6/5 A	05/12/2011	20.8	0.02	60	0.07	23.4	48	0.050	2.4032E-12
		20.8	0.02	60	0.07	23.4	48	0.050	2.9080E-12
ZS1.5 6/5 B		20.6	0.02	60	0.1	23.6	48	0.051	1.6226E-12
		20.6	0.02	60	0.1	23.6	48	0.051	1.6786E-12
ZD1.4 5/8B A		20.8	0.01	60	0.03	20.4	96	0.049	1.1289E-12
		20.8	0.01	60	0.03	20.4	96	0.049	1.0551E-12
ZD 1.45 9/8 A	21/12/2011	22.2	0.025	60	0.03	21.9	24	0.049	2.9023E-12
		22.2	0.025	60	0.03	21.9	24	0.049	2.6183E-12
ZD 1.45 9/8 B		22.1	0.025	60	0.04	21.9	24	0.050	4.5012E-12
		22.1	0.025	60	0.04	21.9	24	0.050	4.2114E-12
ZD 1.4 3/8 A	22/12/2011	22.7	0.05	30	0.063	21.3	24	0.050	1.4320E-11
		22.7	0.05	30	0.063	21.3	24	0.050	1.4635E-11
ZD 1.4 3/8 B		22.5	0.051	30	0.058	20.9	24	0.053	1.5013E-11
		22.5	0.051	30	0.058	20.9	24	0.053	1.4522E-11
ZD1.4 5/8C A	23/12/2011	20.9	0.005	60	0.01	18.9	96	0.051	1.3316E-12
		20.9	0.005	60	0.01	18.9	96	0.051	1.1634E-12
ZD1.4 5/8C B		20.9	0.005	60	0.01	18.8	96	0.049	1.6044E-12
		20.9	0.005	60	0.01	18.8	96	0.049	1.6093E-12
ZD 1.4 5/8B	23/12/2011	22.3	0.01	60	0.025	20.01	96	0.051	2.1738E-12
		22.3	0.01	60	0.025	20.01	96	0.051	1.9600E-12
ZS1.5 6/5 A	27/12/2011	22.1	0.015	60	0.02	22.1	48	0.051	1.9214E-12
		22.1	0.015	60	0.02	22.1	48	0.051	1.8769E-12
ZS1.5 6/5 B		22.1	0.015	60	0.02	22.1	48	0.051	1.9000E-12
		22.1	0.015	60	0.02	22.1	48	0.051	1.9672E-12

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Specimen	test date	init temp, °C	new init Ω, mA	voltage applied, V	final Ω, mA	final temp, °C	test duration	ave LXd	D_{nssm}, m²/s
ZS 1.35 15/7 A	27/12/2011	22.1	0.02	60	0.02	20	48	0.051	1.0273E-12
		22.1	0.02	60	0.02	20	48	0.051	1.0438E-12
ZS 1.35 15/7 A		22.1	0.02	60	0.02	20.1	48	0.052	1.7534E-12
		22.1	0.02	60	0.02	20.1	48	0.052	2.3257E-12
ZD 2.55 25/2 A	07/01/2012	21.6	0.02	60	0.025	20.8	48	0.050	2.35003E-12
		21.6	0.02	60	0.025	20.8	48	0.050	2.30246E-12
ZD 2.55 25/2 A		20.8	0.02	60	0.03	20.4	48	0.050	2.1044E-12
		20.8	0.02	60	0.03	20.4	48	0.050	2.13761E-12
ZD 1.4 5/8A A	07/01/2012	22.1	0.01	60	0.02	20.8	48	0.050	1.31299E-12
		22.1	0.01	60	0.02	20.8	48	0.050	1.35161E-12
ZD 1.4 5/8A A		21.7	0.01	60	0.03	20.3	48	0.048	1.64112E-12
		21.7	0.01	60	0.03	20.3	48	0.048	1.65307E-12
ZR 1.5 29.4 A	09/01/2012	20.4	0.03	60	0.06	22.3	24	0.049	6.06776E-12
		20.4	0.03	60	0.06	22.3	24	0.049	6.04225E-12
ZR 1.5 29.4 B		20.3	0.03	60	0.05	22.1	24	0.050	5.39247E-12
		20.3	0.03	60	0.05	22.1	24	0.050	5.47657E-12
ZS1.4 13/7 A	09/01/2012	20.3	0.005	60	0.01	19.8	98	0.051	8.69483E-13
		20.3	0.005	60	0.01	19.8	98	0.051	8.63592E-13
ZS1.4 13/7 B		20.3	0.005	60	0.01	19.8	98	0.049	1.03538E-12
		20.3	0.005	60	0.01	19.8	98	0.049	1.04161E-12